The Influence of Groundwater Nitrate on the Waimea Stream, Southland, New Zealand

James Michael Thornton

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Abstract

It has long been understood that groundwater and surface water interact, and thus cannot be studied separately. Gaining an understanding of the relationship and connectivity between the two is critical for water management in New Zealand. However, interactions between surface and groundwater are naturally complex, varying both spatially and seasonally due to a multitude of different factors. The aim of this study was to characterise the connectivity between the groundwater of the Waimea Plains in Southland, which has highly elevated nitrate concentrations near the small town of Balfour, and the Waimea Stream, which has also been shown to have elevated nitrate concentrations.

The chemistry of the Waimea Stream was characterised and analysed for significant differences between summer low flows and winter high flows. This was done by first analysing a suite of hydrochemical data collected by Environment Southland between September 2012 and June 2014, then undertaking a monitoring programme from late summer condition to winter (February to July 2016). As well as dominant chemical signatures for winter high flows and summer low flows, spatial and temporal variation in in-stream nutrient concentrations was established. The stable isotopic composition water (δ^2H and $\delta^{18}O$) and DIC (dissolved inorganic carbon) ($\delta^{13}C$) was also analysed.

In both Environment Southland's data and the author's monitoring data, a distinct shift in-stream chemistry was identified between summer low flows and winter high flows. Winter high flows had elevated SO_4, K, B, and Al, concentrations, a Na:Cl ratio similar to that of precipitation and a significantly elevated SO_4:Cl ratio relative to marine aerosols. Summer low flows had elevated Na and HCO_3 concentrations, a significantly elevated Na:Cl ratio relative to that of precipitation, and a diminished SO_4:Cl ratio. Groundwater was shown to exhibit the same chemistry as summer stream water, with a significantly elevated Na:Cl ratio and a low SO_4:Cl ratio. Summer flows are therefore interpreted to be dominated by groundwater, and winter flows are interpreted to be dominantly made up of overland flow and lateral flow through the soil zone.

From δ^2H and $\delta^{18}O$ analysis, the Waimea Plains surface and groundwater appears to be principally sourced from local precipitation. There was no evidence found of any contribution to the Waimea Plains aquifer from the nearby Oreti River. Variation in δ^2H and $\delta^{18}O$ between the headwater and middle reaches of the Waimea Stream suggested that groundwater was contributing significantly to flow in the middle reaches of the Waimea Stream. This was supported by $\delta^{13}C$ analysis which also indicated groundwater connectivity to the Waimea Stream for these same reaches. However, there was limited groundwater connectivity in the lower Waimea Stream, where the strong shift in $\delta^{13}C$ was consistent with DIC outgassing. This may be the result of confining bedrock layers beneath the lower Waimea Stream limiting groundwater contributions to stream water.

In summer, nitrate concentrations in the mid to lower Waimea Stream were significantly higher compared to those in the upper, hill country-fed reaches. Given the findings from hydrochemical and stable isotope analyses, the elevated nitrate over summer in the mid to lower reaches of the Waimea Stream is likely to result from groundwater entering the Waimea Stream in the mid-reaches. Nitrate concentrations are higher throughout the Waimea catchment during winter, although to a slightly lesser extent in the headwaters. Similarly, dissolved reactive phosphorus (DRP)

was elevated over winter. As overland flow is a significant contributor to flow during winter, the winter increase of nitrate and DRP is expected to stem from increased farm run off.

Future management of nutrient inputs into the Waimea Stream should therefore focus on limiting winter surface runoff inputs of both DRP and nitrate. Groundwater inputs of nitrate will be much more difficult to ameliorate, although the use of on farm nutrient budgets should help limit the vertical loss of nitrate down into the Waimea Plains aquifer. Future research should investigate the chemistry of lateral flow soil water directly to better characterise soil water and overland or farm runoff inputs to the Waimea Stream, and hence nutrient fluxes of nutrients into the Waimea Stream from non-groundwater sources

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Chapter 1 Introduction

1.1. Background

Fresh water quality in New Zealand is considered to be good by international standards; however, this varies greatly throughout the country depending on the locality, with local climate, geology, and especially land use contributing greatly to this variability. Living in a country with thriving freshwater ecosystems with rivers that are safe to collect food from and swim in is highly valued by New Zealanders (Hughey, Kerr, & Cullen, 2013; Wright, 2013). Freshwater in New Zealand and the ecosystems they support are also vital to New Zealand's economy, providing a number of services such as clean drinking water, resources for industry including energy generation and agriculture, as well as acting as a sink for the assimilation of wastes from agriculture and industry along with domestic waste (Marie, Stephens, Peart, & Fedder, 2015). Equally important is the intrinsic value of living in a country with healthy and flourishing freshwater ecosystems (Te Ao Marama, 2010).

Declining water quality, especially in lowland streams, has been identified as a developing problem in New Zealand. As a result of data gathered as part of the State of the Environment (SoE) monitoring programme between 1989 and 2007, strong increasing trends in nitrogen and dissolved reactive phosphorus (DRP) have been identified in catchments that are pasture dominated (MfE, 2013). Declining water quality impacts both society as well as natural ecosystems with New Zealand said to rank as one of the worst countries in the world in terms of the proportion of freshwater species that are under threat of extinction (Marie et al., 2015).

The Land and Water Forum was set up in 2009 in response to concerns over New Zealand's fresh water resources. The Land and Water Forum sought input from various community groups and stakeholders on the future of freshwater in New Zealand and how to manage it. Declining water quality across a number of indicators of ecological health and resource value was reported from these forums and three reports were produced which made recommendations regarding how to tackle freshwater quality and quantity declines. Following on from this, the National Policy Statement for Freshwater Management was created (MfE, 2014). This set a number of limits and bottom lines for water quality and quantity and directed regional councils to create plans to manage local freshwaters accordingly.

The National Policy for Freshwater Management has stated that water bodies need to be protected, and restored if necessary, so as to safeguard 'the life-supporting capacity, ecosystem processes and indigenous species including their associated ecosystems, of fresh water' (MfE, 2014). It is of note that the connection between water bodies is recognised as being critical. Regional Councils are thus required under Policy A1 to set fresh water objective that have regard for the connection between water bodies'. This is important as it recognises the impact hydrologically connected water bodies may have on one another, including connectivity between surface and groundwater. Having a good understanding of the dynamics of any possible connections between water bodies and the fluxes of contaminants between different waters is essential for developing specific policies and plans for catchment water and land use.

The Southland region has over the last couple of decades seen an intensification of farming practices (Monaghan, Semadeni-Davies, W Muirhead, Elliott, & Shankar, 2010). For most of the 20th ceFAUry sheep farming dominated the Southland rural landscape, however, a recent shift has occurred towards high nutrient loss land uses such as dairy farming and winter cropping. In 1984 a peak of over 9 million sheep was reached. Since then stock intensity has not increased with overall stock numbers remaining at around 9 million. Nevertheless, over this period dairy cow numbers have increased from 46656 in 1990 to 614648 in 2011. This corresponds to an increase in dairying from 23000 hectares in 1992 to 196000 hectares in 2011 (Ledgard, 2013). From this there has been observed an increase in the pressure on the region's water resources and indications that declines in water quality are occurring across the region (Ledgard, 2013).

Historically, the main focus of water quality issues in Southland was sedimentation from land clearance and development, as well as pollution from point source discharges from industry, community wastewaters and agricultural effluents. Point source discharges have been largely controlled through, for example, the better treatment of industrial and community wastewaters as well as through improved practices, such as discharging agricultural effluents onto land rather than directly into waterways. The key driver of water quality decline in Southland today has changed and is associated more with non-point discharges which are contributing sediments, faecal bacteria and nutrients to waterways (Snelder et al., 2014). Diffuse pollution is where the contaminant does not come from any one particular defined source such as a drain, but is rather thinly spread across a large area, such as nitrates leaching through soil into groundwater, making it much more difficult to identify and ameliorate.

Environment Southland's (Southland Regional Council) Regional Water Plan 2010 sets out a number of water quality issues and targets for the following decade (Environment Southland, 2010). The first priority is to see no further degradation of surface water quality. A specific target of improving surface water quality has been set whereby there should be a 10 percent reduction in nitrate and DRP concentrations, as well as a 10 percent improvement in water clarity by 2020. The plan also aims to see water quality maintained and enhanced so as to support trout, native fish, stock drinking water, and Ngai Tahu cultural values including Mahinga Kai. A critical part of this strategy involves gaining a greater understanding of the connectivity between ground and surface waters, an hence the degree to which the latter influences the former.

1.2. Research Aims

1.2.1. Aim

The aim of this study is to investigate whether elevated groundwater nitrate concentrations found near Balfour on the Waimea plains are responsible for the elevated in-stream nitrate concentrations observed in the Waimea Stream, Southland, New Zealand.

1.2.2. Approach

In-stream flow typically varies throughout the year. As flow varies the relative contribution to in-stream flow of groundwater, which tends to dominate low flows, and surface runoff (overland flow), which tends to dominate high flows, will also vary. Low groundwater dominated flows tend to dominate during the dry summer months, while overland/surface runoff dominated flow tend to dominate during the wetter winter months.

In order to determine the relative contribution of groundwater-fed base flow to in-stream nitrate concentrations this study will firstly investigate the hydrochemical character of summer base flows

and winter high flows. From this the chemical character will be established of summer and winter end-members (groundwater dominated base flow Vs overland flow dominated high flows).

In-stream nutrient concentrations will be analysed over the same period between summer low flows and winter high flows. The chemical signature of the groundwater and overland flow end-members will then be related to in-stream nitrate concentrations in order to establish which end-members dominate when in-stream nitrate concentrations are elevated.

1.2.3. Objectives

(i) Characterise the in-stream chemistry of summer base flows and winter high flows
(ii) Determine the level of, and rate of change of, a number of groundwater derived components (e.g. iron, manganese, dissolved inorganic carbon (DIC) and other possible tracer elements and isotopes) through a transition period from summer to winter flows.
(iii) Determine the monthly concentration and rate of change of nitrates in-stream through a transition period from summer to winter flows, along with DRP.
(iv) Determine whether nitrate concentrations decrease from summer to winter as the stream moves from groundwater dominated base flow to an overland flow dominated flow.
(v) Analyse data to determine whether there is a correlation between changes in nitrate concentration from summer to winter, and the chemical character of the groundwater and overland flow end-members identified.
(vi) Examine $\delta^{18}O$ and $\delta^{2}H$ to assess the origin of surface water in the Waimea Stream
(vii) Examine longitudinal profiles of $\delta^{13}C$-DIC, $\delta^{18}O$ and $\delta^{2}H$ for evidence of groundwater contributions to in-stream flow.

1.3. Groundwater and surface water processes

In this section the key processes of ground and surface water relevant to this study are described. Firstly, groundwater-surface water interactions are covered. Secondly, nutrients and the pathways by which they enter streams are described along with the process of eutrophication. Thirdly, the processes and interactions that influence the chemistry of water bodies is explained, and finally, the theory behind the use of stable isotopes and other chemicals as hydrological tracers.

1.3.1. Ground water-surface water interactions

Rainfall that falls on the earth's surface can take one of two basic flow paths. It can either run directly across the surface and into streams, in what is termed overland flow, or water can penetrate the earth's surface and seep underground. Water will then move both vertically and laterally underground. This is the water that constitutes aquifers, or groundwater. Where and how the water will flow and at what speed depends on a large number of factors such as topology, the local substrate and how permeable it is.

Recharge moves along either rapid or slow flow paths and can be sourced either locally or can from rain that fell at a distance. Rapid flow paths include overland flow that occurs for example in alpine or hilly country whereas a slow flow path is the gradual percolation of water through the unsaturated zone into an aquifer. Bypass flow is another type of rapid flow path whereby water moves rapidly through the soil zone via either natural features such as cracks or through artificial structures like mole tile drainage systems. Recharge flow paths can also be categorised by whether they are distal or local. Distal recharge is where the source of recharge is from precipitation that fell in a different domain and travelled some distance to where the recharge occurs (riverine recharge).

Local recharge is where the source of recharge is from precipitation that has fallen locally (land surface recharge) (Rissmann et al., 2016c).

Groundwater exists beneath the earth's surface in two main zones known as the saturated and the unsaturated or vadose zone. The unsaturated zone sits between the land's surface yet above the saturated zone. This is where the voids or cracks in the soil, gravel, clay, silt or rock contains water but also contains air, hence it is unsaturated. The upper most part of the unsaturated zone is known as the soil-water zone. This is where there are plant roots, worm and animal burrows as well as cracks caused by drying, all features that enhance the infiltration of water into the unsaturated zone, and on through to the saturated zone. The depth of the unsaturated zone can vary from a few centimetres to hundreds of metres. In the unsaturated zone the water cannot be pumped for example as the water will be held back by capillary forces. Within the saturated zone on the other hand, these voids are completely occupied by water. This is water that can be pumped to the surface (Winter, Harvey, Franke, & Alley, 1998a). The level of the saturated zone is also known as the water table (Figure 1-1).

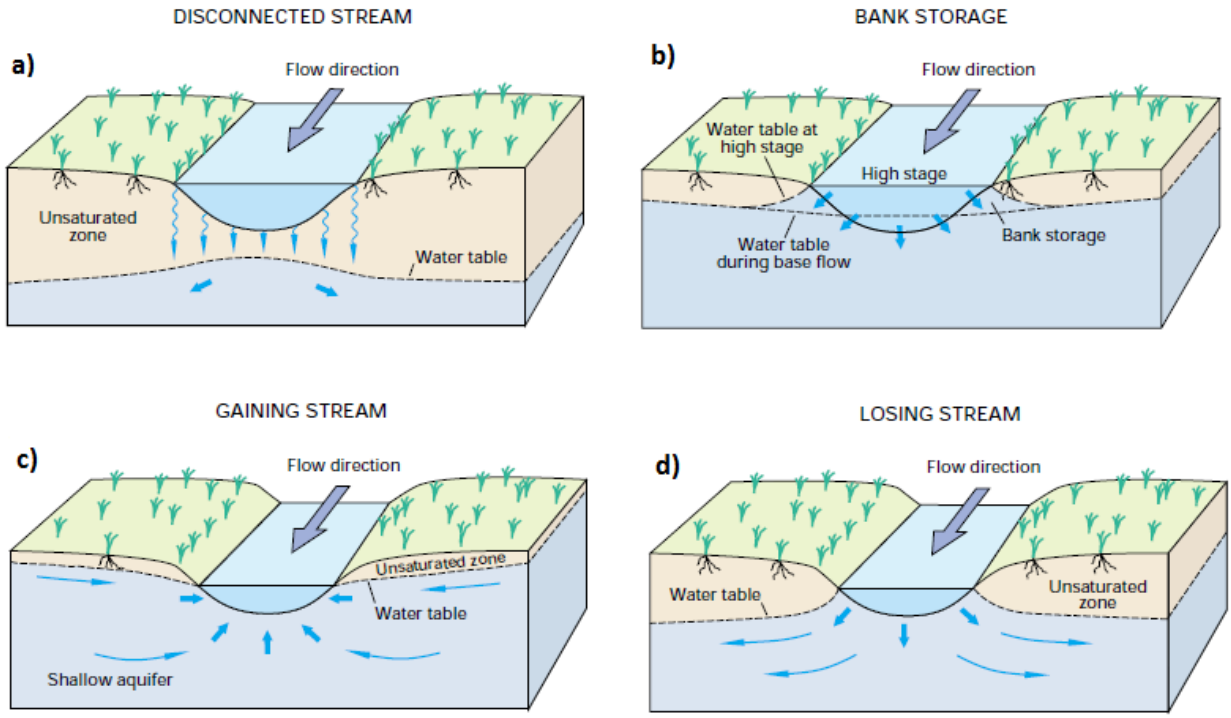

Figure 1-1 Surface water-ground water interactions for a) surface water discounted from groundwater and losing water to ground water, b) high stream flow losing flow to groundwater and contributing to short term 'bank storage', c) surface water gaining water from groundwater, d) surface water connected to, and losing water to, groundwater. Diagram adapted from (Winter, Harvey, Franke, & Alley, 1998b).

Any point at which the saturated zone reaches the surface is where groundwater emerges and interacts with surface water bodies, producing springs. It is thought that groundwater provides some 40-60% of the flow to surface waters across Southland (Rissmann, 2012). A number of factors can influence where and how the saturated zone emerges to the surface, with confining layers such as clay and rock potentially inhibiting groundwater from reaching the surface, despite the water table meeting or being very close to the lands surface. The subsurface zone where surface water and groundwater actively mix is known as the hyporheic zone. Because the hyporheic zone is where groundwater and surface water actively mix the chemical character of the hyporheic zone may differ substantially from that of either the ground or surface water itself.

Streams interact with groundwater in two principal ways, by either losing water to groundwater, which is known as a losing stream, or gain water from ground water, which is known as a gaining stream (Figure 1-1). Whether a particular reach of a stream gains or loses water will depend on the local depth of the water table, as well as the presence or absence of any confining layers. As a result of the variability in these factors, a single stream may gain or lose water at various points along its course. For example, although a section of stream may be down gradient of where the water table reaches the surface, confining layers of bedrock may prevent connectivity between ground and surface water.

Streams can be completely disconnected from the water table by the unsaturated zone. In this case the stream will lose water via seepage through the unsaturated zone. When the water table is connected to a stream this can provide a base flow which can maintain a stream's flow even during periods of little rainfall. Another important interaction can occur through bank storage. This is where periodic high flows such as flood events or snow melt leads to seepage in to the stream's bank, raising the local water table immediately adjacent to the river (Figure 1-1b). This water then will gradually discharge back into the river over the subsequent days and weeks. Such bank storage will tend to diminish extreme flows and maintain flow levels between flooding events (Winter et al., 1998b).

A stream, especially in its headwaters, can switch between gaining and losing conditions. For example, a stream may be completely dry during dry periods, and only flow during wet periods or storm events, losing water into the unsaturated zones during these events. However, during prolonged wet periods the water table may rise above the level of the stream bed in which case the stream may switch from a losing stream to a gaining stream. Thus, in these reaches, groundwater inputs to flow may be proportionally greater during wet periods, rather than during prolonged dry periods, as may be the case in the lower reaches of a stream.

1.3.2. The role of nitrogen and phosphorus

Both nitrogen and DRP are essential nutrients to life on earth. However excessive amounts can lead to the excessive growth of aquatic plants and algae in-streams, including the growth of toxic algae and cyanobacteria. Nitrogen and DRP in-streams can be sourced from natural sources such as litter fall, oceanic upwelling, and weathering, but can also be sourced from human activities including sewage, leaching from cleared land, fertilizer runoff, agricultural effluents as well as industrial effluents (ANZECCa, 2000).

Nitrogen exists in a number of forms that are available for plant growth, including nitrate (NO_3), nitrite (NO_2), ammonia (NH_4) and organic forms such as urea which is a breakdown product of proteins. Reactive nitrogen is essential for plant growth. Historically the world's ecosystems have existed in nitrogen-limited conditions, and have evolved under conditions of competition for available nitrogen (Galloway & Cowaling, 2002). To promote the growth of vegetation on farms nitrogen fertilisers are used by farmers. Nitrogen that is applied to a paddock can, under the right conditions, leach through the underlying soils and enter the groundwater. Nitrate generally travels relatively freely through soils, and unlike phosphate which tends to adsorb or stick to the surface of soil particles, moves at roughly the same rate as water, as it percolates down through the soil layers (Freeze & Cherry, 1979). This means that excess nitrogen in the soil/plant system can, under the right conditions, travel down through the unsaturated or vadose zone and into the groundwater system.

Nitrates can also travel directly into surface water systems through overland flow. Such movement can be enhanced by artificial drainage networks such as mole pipe systems. Artificial drainage

systems can intercept the downward movement of subsurface flow and deliver nitrates directly to surface water systems. Such drainage networks are also capable of facilitating the transport of less mobile contaminates such as DRP, sediment and E.coli to surface waters (Monaghan et al., 2010).

The amount of nitrogen that leaches into groundwater depends on a number of factors such as the amount of nitrogen fertilizer applied, the level of plant uptake of nitrogen, the amount of nitrate in the soil and the amount of soil drainage that occurs over a given period. For example, nitrate leaching rates are often higher during winter due to higher rainfall and a lower rate of evapotranspiration, coupled with lower levels of nitrate uptake through plant growth. The amount of drainage that occurs is important with higher nitrate losses occurring from sandy soils compared to clay soils for example. Macropore features such as those created by worms or plant roots, as well as cracks formed by excessive wet and dry cycles can enhance drainage and therefore the leaching rate (Cameron, Di, & Moir, 2013).

Nitrate entering groundwater can pose a direct risk to human health. Water with nitrate concentrations sufficiently high can become unsafe for human consumption or for use as stock drinking water. During the middle of the 20th ceFAUry it was recognised that high levels of nitrate in drinking water may pose a health risk, especially to young babies. High nitrate concentrations can cause a condition known as methaemoglobinaemia (Ward et al., 2005). This is where nitrate, when converted to nitrite in the human body, binds to the oxygen carrying haemoglobin in the blood supply, converting it to methemoglobin. This renders the haemoglobin affected unable to carry oxygen through the blood supply. Reduced oxygen supplies can lead to a bluish pigment in the skin, and in severe cases can result in death. A more common name for the disease is 'blue-baby syndrome' (Rosen, 2001). The World Health Organisation has set a drinking water guideline value of 11.3 mg/L (NO_3-N) of nitrate (WHO, 2011).

Phosphorus can be present in water in either a dissolved or particulate form and behaves differently to nitrate. In particulate form phosphorus is bound to suspended particles including clays and other detritus such as decaying organism as well as organic compounds such as proteins. The dissolved form includes inorganic orthophosphate (H_2PO_4), polyphosphates, as well as organic colloids and phosphate esters (ANZECCb, 2000). The main reservoir of phosphorus, unlike nitrogen which is abundant in the atmosphere, is in sediments and rock. Phosphorus is slowly released through weathering processes, and in unpolluted river the metabolic demand for phosphorus will often far exceeds supply. A principal route by which phosphorus enters waterways is through the flushing of phosphorus bound to sediments off of paddocks during wet periods. There is debate regarding which is the best form to measure that will represent the impact on a stream's ecology. Dissolved reactive phosphorus (DRP) is often measured as this is most readily available to organisms, however, as there is often rapid cycling between this form and the bound forms, it is possible that recording just the dissolved form may not capture the true picture of what is available to the ecosystem (Allan, MCastillo, & Maria, 2007)

1.3.3. Eutrophication of streams

Eutrophication is the process where, due to high levels of nutrients in a stream, in particular nitrogen and phosphorous, primary producers such as marcophytes (aquatic plants) and periphyton (algae) undergo excessive levels of growth (Allan et al., 2007; Davies-Colley & Wilcock, 2004). A stream with such nuisance growth will appear clogged with macrophytes and high levels of algae or periphyton. Such nuisance growth can result in a number of issues. High levels of macrophytes and periphyton can lead to the clogging of the stream which can impact fish migration, smother habitat for various species, as well as affect water intake structures. Indeed, highly elevated nitrate concentrations can be directly toxic to aquatic organism. A reduction in the water quality in terms of

pH and dissolved oxygen as a result of the decay of excessive organic material can lead to fish kills (Biggs, 2000b). An overall shift in the biodiversity of a stream can result from this. For example, endemic species such as flagellates can be replaced by diatoms. Such changes can also impact aesthetic and recreational values of a stream, for example a stream may no longer be suitable for drinking from or indeed swimming in due to the presence of toxins produced by cyanobacteria (ANZECCb 2000).

Only moderately elevated concentrations of nutrients in surface waters can lead to the nuisance growth of algae and macrophytes. For example, total nitrogen needs to be below 0.4-1.0mg/L (NO_3-N) and total phosphorous needs to be below 0.15-0.30 mg/L (PO_4-P) for nutrient levels to have a significant impact on controlling the level of periphyton growth. The trigger values set in the ANZECC guidelines for nitrate is 0.614 mg/L (NO_3-N) and dissolved reactive phosphrorus is 10 µg/L (PO_4-P) for moderately disturbed lowland rivers (defined as <150m elevation). This trigger value is given as a general guideline for management purposes. The specific circumstances of a given stream will determine how it responds to increases in nutrient concentrations, meaning that some rivers may have much higher nutrient levels and yet remain relatively unaffected, whereas other streams may be severely impacted with nutrient values close to the trigger value (ANZECCa, 2000).

In algae and cyanobacteria the intracellular atomic ratio of C:H:O:N:P:S approximates 106:263:110:1:0.7. This ratio is mirrored by the approximate uptake of nutrients by growing populations and is known as the Redfield ratio, which for nitrogen and phosphorus is 16:1 (Redfield, 1958). Consequently, a stream's ecosystem can be said to be either limited in nitrogen or phosphorus depending on the N:P ratio. For example, a N:P ratio < 16:1 is said to be nitrogen limited, while a ratio > 16:1 is said to be phosphorus limited. This ratio can however be misleading as it has been found that different species are limited by different N:P ratios. In addition, a measurement of the dissolved phosphorus and nitrate available in-stream at any particular point may not account well for the overall availability of nutrient to an ecosystem (Allan et al., 2007). This is because the actual flux of nutrients through a system is not accounted for. For example, large stores of nutrients may be bound up in surrounding substrate which is readily released during higher flows.

How a particular stream actually responds to elevated nutrient concentrations depends on three crucial factors, the concentration and ratio of total nitrogen and phosphorous, the flow regime, and the levels of light available (Allan et al., 2007; ANZECCa, 2000; Biggs, 2000a). The flow regime is particularly important as flooding events will act to flush out nuisance growth (Biggs, Goring, & Nikora, 1998). Thus the periods between flood events, or accrual time, is crucial in determining how much nuisance growth will occur. Other factors such as stream substrate (rocks, cobbles, sediment) are also important, with stony stream beds being more amenable to the growth of periphyton for example, than streams with sandy substrates. Finally, the amount of light, and hence the capacity for photosynthesis to occur is critical with the amount of riparian shading is thus also of critical importance in determining how a stream will respond to elevated nutrient levels. The level of turbidity present is another crucial factor in determining the amount of light available for photosynthesis to occur.

Due to the connectivity between groundwater and surface water, when a stream ecosystem is nitrogen-limited, high levels of nitrogen in groundwater can contribute to the eutrophication by contributing water high in nitrates. The concentration of nitrates when released from groundwater into a stream tends to be lower than that in the groundwater itself. This is due to the effects of dilution in-stream, although this will depend on the proportion of ground to surface water derived flow (Rissmann, 2012). However, the concentrations at which elevated nitrates can lead to declines in water quality in surface water are significantly lower than that at which it become problematic in groundwater. Significantly, groundwater can provide nutrients to surface waters over summer when

conditions are ideal for macrophyte and periphyton growth in terms of an abundance of sunlight with few flood flows that would act to flush out nuisance growth.

1.3.4. Hydrogeochemistry

The chemical properties of surface and ground waters can be used to characterise both inter and intra catchment surface water and groundwater interactions (Davies-Colley & Wilcock, 2004). Nearly all groundwater has its origin in precipitation before it enters the soils and flow systems of the local geology. As water moves through the ground it is altered chemically through its interactions with soils and rocks and through various chemical processes. Both the precipitation and the unique interactions with and areas geology impart a distinctive chemical character to a water body that can be useful for tracing the water origin and its flow paths. These hydrochemical dynamics are driven by fluctuations in various natural processes and settings along with anthropogenic influences (Kendall & McDonnell, 1998). These influences on hydrochemistry include the local climate, topography, the composition of the regions substrate in terms of soil, rock and biology, the mechanism and source of recharge as well as an areas land use and management. These mechanisms influence the solute concentration of a given stream by varying precipitation, isotopic fractionation, sorption, ion exchange as well as redox reactions.

These drivers of hydrochemistry fluctuate seasonally with different patterns of drivers resulting in distinctive hydrochemical signatures. For example, the nature of surface inputs in a stream will vary depending on where the precipitation in the catchment fell, along with the flow path the water undertakes on its way to a stream. Thus, at any particular time surface flow is a mix of multiple end-members that vary seasonally. For example a catchment may have three principal pathways whereby water enters a stream:

1. Groundwater inputs that make up the stream base flow.
2. Overland inputs from precipitation collected on lowland country
3. Hill country or alpine overland inputs.

These three end-member waters have distinctive pathways through the environment and hence distinctive hydrochemistry. By looking at surface flow under different hydrological conditions is possible to determine the chemical character of these different end-members. For example, 1 may dominate over summer during very low flow conditions, while 2 and 3 may dominate during very high rainfall events over winter. Most of the time however neither end-member may dominate a stream's chemistry, rather, all three will be imparting their distinctive chemistry onto the stream, resulting with an in-stream chemistry that is a mix of all three end-members.

Overland flow from hill country or alpine sources will for example tend to have a lower marine aerosol influence along with different isotopic signatures to lowland overland flow. Groundwater dominated base flow often has higher levels of solutes. As a result of this surface flow solute concentration will often be inversely proportional to flow as groundwater inputs come to make up a greater or lesser proportion of surface flow (Hem, 1985). However, for the Southland region it has been found that surface recharge tends to dominate surface water chemistry (Rissmann et al., 2016a). A key reason for this the relative rate of weathering between that of the soil zone and that of rock weathering in the saturated zone. The latter occurs at a much slower rate than the former. This is due to the ions within the soil zone being much more readily released and flushed into a stream than solutes from rock into groundwater. Ions within the soil zone are more loosely bound than those in rock, and hence are much more readily released. Thus, lateral flow through the soil matrix in Southland's case has been found to dominate stream chemistry (Rissmann, 2012)

Major ions

The chemistry of surface and groundwater principally concerns eight major ions which generally make up approximately 95% of waters ion content. The positively charged ions are sodium (Na), potassium (K), calcium (Ca), and magnesium (Mg). The negatively charged ions are chloride (Cl^-), sulphate (SO_4), bicarbonate plus carbonate (HCO_3 + CO_3). Taken together these species make up most of the 'total dissolved solids' of water which can be approximated by measuring the water's electrical conductivity. The solutes in freshwater originate from two principal sources (Cook and Herczeg 2000):

1. Atmospheric precipitation- marine salts and continental dust.
2. Water rock interactions.

The solutes contained within water can tell a story about the water's history, its origin, where it has been and for how long. Once within a drainage basin there are two major controls of water chemistry, the type of geological materials present, and the length of time the water is in contact with these materials.

Rainfall contains solutes through aerosols that become dissolved in the precipitation. As a result of originating from the ocean, precipitation tends to reflect the chemical composition of the ocean, and can thus be considered to be dilute seawater (Hounslow, 1995). Rainfall that occurs near the coast therefore will maintain this original chemical composition, in particular a high Mg/Ca ratio as well as high levels of the marine solutes Na and Cl. Rainfall that occurs further inland will have a slightly different composition as the marine solutes fall out in conjunction with the gradual acquisition and dissolution of continental dust, resulting in elevated levels of Ca and SO_4. In addition, industrial gases such as NO_x and SO_x can be accumulated in rainfall, which can produce strong acids and thus lead to acid rainfall (Cook & Herczeg, 2000). New Zealand is a relatively small island and hence precipitation is dominated by marine weather systems that are relatively high in Na and Cl (Verhoeven, Herrmann, Eiden, & Klemm, 1987). In general rainfall is a relatively dilute, oxidising solution that will readily react with the geologic materials it comes in contact with once it infiltrates the land's surface (Freeze & Cherry, 1979).

Once rainfall has fallen, it enters the terrestrial hydrological cycle where firstly it undergoes evopotranspiration. This is where through evaporation and the uptake of water by plants an increase in ion concentrations occurs. This process can lead to ion concentration of an order of magnitude greater than that of the original rain water in situations where potential evaporation exceeds the level of precipitation (Cook & Herczeg, 2000). Water at this point will either run across the ground's surface or leach into the ground. Surface runoff still interacts with the soil zone as it travels overland. The reactions that occur are significant enough to make the dissolved solute concentration of direct runoff still significantly higher than that of the original rainfall (Hem, 1985).

When water enters the soil zone it interacts with soils high in microbes and organic matter. These microbes break down the organic matter, raising the concentration of dissolved carbon dioxide which leads to a lowering of the soil pH as a result of higher levels of carbonic acid (H_2CO_3). The decomposition of organic materials produces an array of acids including oxalic and acetic acids as well as other acids such as formic and malic acids (McSween, Richardson, Uhle, & Richardson, 2003). Carbon dioxide generation tends to follow a seasonal pattern which reflects shifts in temperatures as well as soil moisture. During spring and the growing season soil CO_2 levels rise rapidly, before declining at the end of the growing season (McSween et al., 2003). Carbonic acid production stimulates mineral weathering reactions resulting in elevated ion concentration, in particular of inorganic carbon species including carbonate (CO_3) and bicarbonate (HCO_3) (Cook & Herczeg, 2000; Winter et al., 1998a). The oxidation of reduced iron minerals such as pyrite (FeS_2) also acts as a

source of acidity. Production of H^+ from such oxidation reactions in some areas can play an key role in promoting mineral weathering (Freeze & Cherry, 1979). During the course of rock weathering the ions Ca, Mg, SO_4, HCO_3 and SiO_2 is added to the water. How much of each ion depends on the local mineral content with which the water interacts (Hounslow, 1995).

The amount of contact time groundwater has with the local geology can vary from a couple of years to in some case millennia. Water that has short underground resident times will have little contact time with minerals and will hence generally have lower ion concentrations. If this is the case the scale of chemical changes that will take place to the water will be limited before the water is discharged to the surface. In comparison, water that spends significant lengths of time underground interacting with the local geology will show greater signs of chemical change. As a general rule, the greater the length of time water spends underground, the greater the change in terms of attaining higher levels of solutes through water rock interactions, although the overall amount of solute acquisition will also depend on how weatherable the local rock material is.

Different major ions are sourced from different minerals and processes (Table 1-1). For example, a major source of sulphate can be pyrite and gypsum, while major sources of bicarbonate includes atmospheric CO_2, sulphate reduction and pyrite oxidation. Thus, the major ion composition of freshwater can indicate what materials and processes that water has been through and what kind of geological materials it has had contact with.

Table 1-1 Sources of major ions in surface and groundwater (Hounslow 2005).

Ion	**Source**
Sodium	Halite, albite
Potassium	Mica, potash, feldspar
Calcium	Calcite, dolomite, gypsum, anorthite
Magnesium	Ferromagnesium, silicates
Chloride	Brine, seawater, rainwater, halite
Sulphate	Pyrite, gypsum
Bicarbomate	Atmospheric CO_2, sulphate reduction, pyrite oxidation.

The chemical composition of groundwater can be described and categorised into different water types or hydrochemical facies. This is essentially a description or characterisation of which ions are most dominant within a water body. Major ions are plotted using a piper diagram which can be used to sort groundwater into different classes (Figure 1-2) (Piper, 1944). Groundwater as it travels underground tends to evolve towards the composition of seawater. Younger groundwater tends to be dominated by HCO_3, while groundwater of a more intermediate age will tend to be dominated by SO_4^{2} ions and will have higher levels of dissolved solids. Finally, groundwater that is older still will have even higher levels of dissolved solids, and will tend to be dominated by Cl ions (Rosen, 2001; Younger, 2007). Although these characteristic give an indication of relative age and travel time they cannot be correlated with specific ages and travel times (Freeze & Cherry, 1979). The most common type of water in New Zealand is Ca-Na-HCO_3 dominated solutions as well as Ca-HCO_3 solutions. HCO_3 has been found to be the most common dominant anion in New Zealand groundwater, while chloride has been found to dominant in some wells (Rosen, 2001). This reflects the fact that New Zealand's groundwater tends to be relatively young and near the surface and are thus exposed to the interaction of dissolved CO_2 from the atmosphere with organic matter and the subsequent washing down through the soil of HCO_3 which leads to enhance rock weathering.

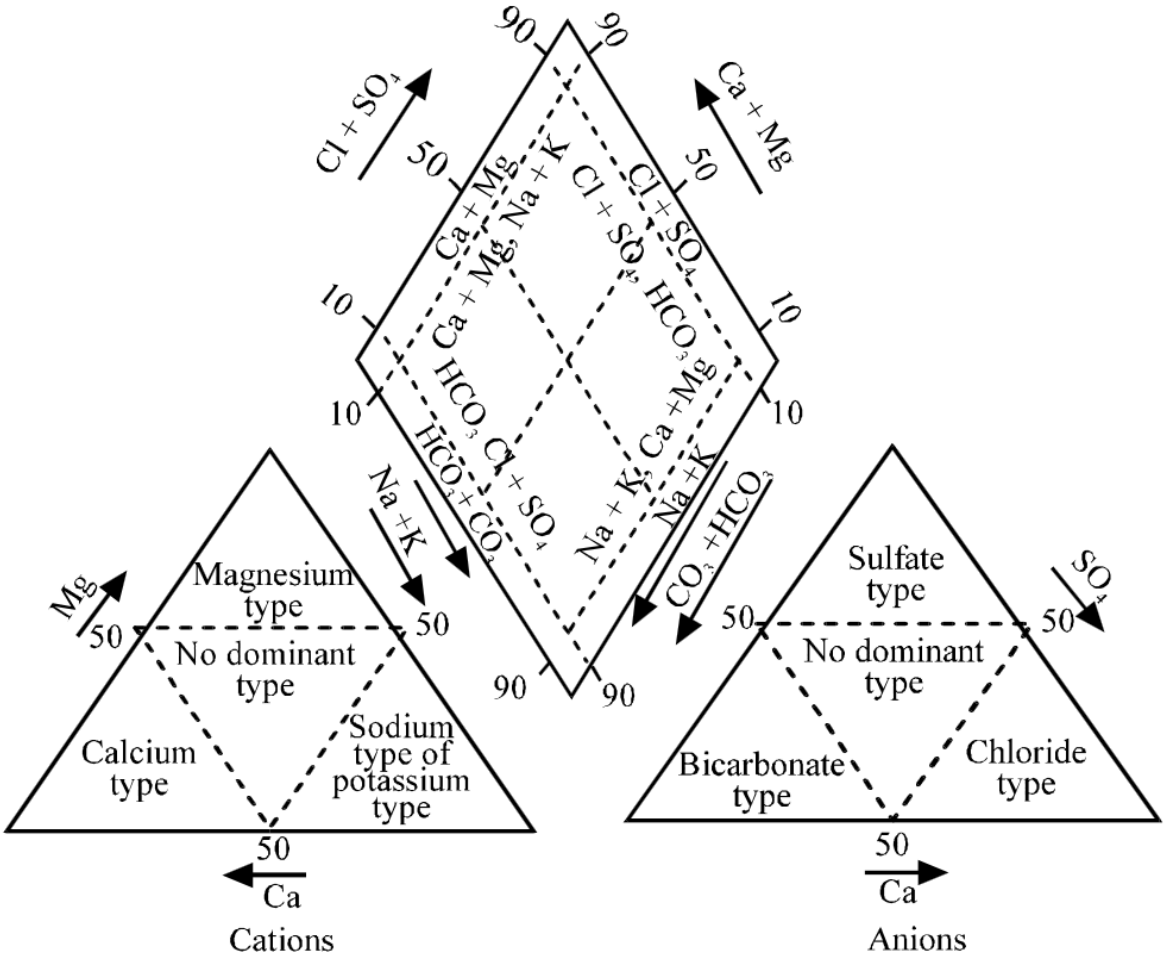

Figure 1-2 Trilinear Piper diagram for discerning water facies. Ion concentrations are displayed in % meq. The bottom left triangle displays the water composition by major cations, the bottom right by major anions. The diamond on top displays the water composition as a combination of both major cations and anions (Piper, 1944).

1.3.5. Weathering reactions and processes

Within the environment chemicals can exist in one of several different pools (Shuman, 1991). They can either be:

1. Dissolved
2. Occupying exchange sites or adsorbed to inorganic elements/molecules
3. Adsorbed to organic matter
4. Precipitated as pure or mixed solids
5. Present as primary or secondary minerals

The form that elements take (speciation), and thus the pool they are found in, significantly affects the transport of elements through the soil zone, as well as the kind of reactions or processes that would occur during the weathering of that particular element. For example, different complexes of trace metals can result in species that can be either positively or negatively charged, or indeed neutral (e.g. $CdCl_3^+$, $CdCl_2^0$, $CdCl^-$) (McLean & Bledsoe, 2009). This affects movement through the soil zone by impacting the degree to which trace metals will bind to or adsorb to clay particles, which are generally negatively charged. Speciation also affects the bioavailability and toxicity of metal ions, with free ions (e.g. Cd^{2+}) generally being the most toxic or bioavailable form.

Dissolved chemicals are defined as being able to pass through a 0.45µm filter. Chemicals may also associate with larger colloidal particles such as iron and manganese oxides, along with organic matter and clay minerals. Colloidal particles, which have a high capacity for trace metal adsorption, can facilitate the transport of trace metals from the soil zone and into streams, especially during wet periods of high flow during which large amounts of sediment is flushed into streams via overland flow. This is known as 'facilitated transport'.

Chemical reactions will affect the relative proportion of different species of chemical substances within a water body. Many of these are weathering processes that involve water and either an acid or oxygen in the decomposition of geological materials (McSween et al., 2003). A number of reactions can alter the chemical makeup of water (Table 1-1), these include the precipitation and dissolution of minerals, acid-base reactions, sorption and ion exchange, redox reactions, biodegradation and the dissolution and exsolution of gases (Winter et al., 1998a).

Ion exchange and adsorption

Ion exchange and adsorption is the process whereby ions interact with colloidal-sized particles. Colloidal particles are small particles ranging from 10^{-3}-10^{-6} mm in diameter that are found in clays, weathered rocks and sands. The particles have an uneven surface with an electrical charge which attracts and binds free ions which counter the charge imbalance on the colloid's surface. Such bound ions can be exchanged for other ions in solution so long as the colloid's charge is balanced. The colloid's surface charge is related to pH with a high pH resulting in a negative charge, while a low pH will produce a positive charge (Freeze & Cherry, 1979). The degree to which ions can bind to colloidal particle varies, from weak binding (adsorption) to stronger binding (ion exchange). The former is where ions bind to weak binding sites on the surface of colloidal particles, while the latter is where ions migrate into the pores and undergo solid-state reactions leading to higher energy binding sites (Laing, Rinklebe, Vandecasteele, Meers, & Tack, 2008). Weakly bound ions will be much more readily released than those that are bound to higher energy binding sites. The capacity soils have for binding cations is known as the cation exchange capacity (CEC). More negatively charged soils will have a greater CEC and will hence reduce the mobility of positively charged ions through the soil zone (Evans, 1989).

Dissolution reactions

As water comes into contact with minerals dissolution will separate the mineral into its constituent ions. This is the process whereby decomposition agents such as carbonic acid, H_2O and humic acid interact with rocks and is a major source of inorganic elements in water (Hounslow, 1995). This will continue until equilibrium concentrations are reached in the water or all the minerals have been consumed. Different minerals have vastly different solubilities (Freeze & Cherry, 1979). Groundwater that comes into contact with minerals with very low solubilities may only have dissolved content similar to rain water, whereas if it comes into contact with highly soluble minerals it may accumulate very high levels of solutes. The dissolution of calcite is an example of a dissolution reaction:

$$CaCO3 = Ca2+ + CO32-$$

Equilibrium reactions

Equilibrium reactions between dissolved chemicals lead to changes in solution chemistry. An example of an important equilibrium is CO_2 dissolving in water to form carbonic acid (H_2CO_3). Carbonic acid then dissociates to produce bicarbonate (HCO_3^-), carbonate (CO_3^{2-}) and hydrogen ions (H^+). The concentration of each of these species is controlled and related through equilibrium

reactions and pH (Figure 1-3). Most New Zealand waters sit within a pH range of 7-8, and this is reflected in bicarbonate being the most dominant inorganic carbon species.

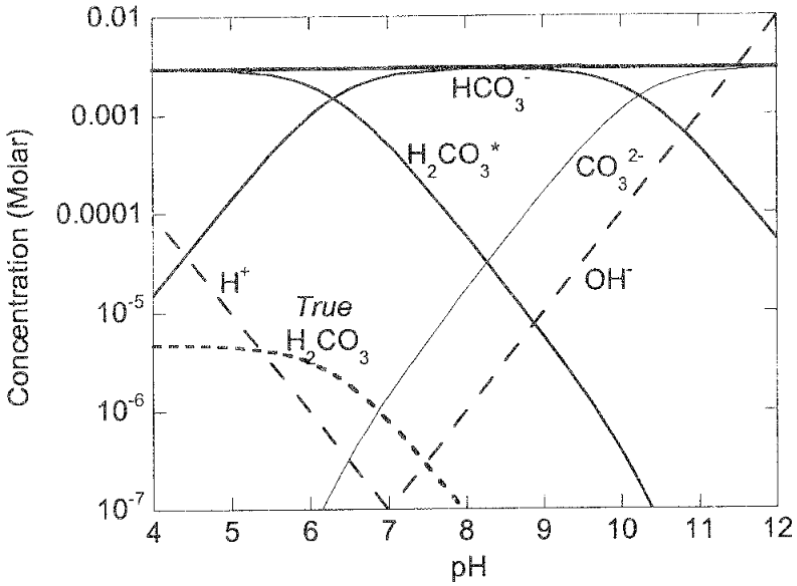

Figure 1-3 The distribution of inorganic carbon species in water showing the relative concentration of different DIC species at 3 X 10^{-3} M DIC under different pH conditions (Davies-Colley & Wilcock, 2004).

Redox reactions

Redox reactions and the redox state of water, in particular groundwater which is isolated from the atmosphere, plays an important role in determining the composition and chemical nature of water components. Redox reactions involve the transfer of electrons between different chemical constituents. Iron is a redox sensitive chemical which, for example, will take on different redox states depending on the redox state of the water. Free iron(II) will be oxidised to iron(III) by oxygen:

$$\begin{array}{l} \tfrac{1}{2}\, O_2 + 2H^+ + 2e^- = H_2O \text{ (reduction)} \\ 2Fe^{2+} = 2Fe^{3+} + 2e \text{ (oxidation)} \\ \hline 4Fe^{2+} + O_2 + 4H^+ + 4e^- = 4Fe^{3+} + 4e^- + 2H_2O \end{array}$$

Surface waters tend to have oxidising conditions due to their constant mixing and exchange with atmospheric oxygen. Groundwater on the other hand are isolated from the atmosphere and tend towards developing reducing conditions as oxygen becomes depleted (Freeze & Cherry, 1979). The extent to which oxygen in groundwater becomes depleted depends largely on the presence and subsequent oxidation of organic matter, which is facilitated by microbes or isolated enzymes. These microbes or isolated enzymes drive the electron transfer process forward, oxidising carbohydrates until groundwater oxygen is depleted and the redox state shifts. Once groundwater is anaerobic oxidation can still occur but the oxidising agent shifts to the next strongest oxidant in the following order NO_3 > Mn > Fe > SO_4 (Freeze & Cherry, 1979). This has important consequences for nitrates in groundwater. Groundwater low in organic matter will tend towards oxic condition and will hence maintain and accumulate any nitrate inputs such as leachate from agricultural land. On the other hand, in anaerobic groundwater nitrates can potentially be reduced to nitrogen gas which will subsequently be released to the atmosphere in a process known as denitrification. Such groundwaters are less sensitive to nitrate accumulation.

1.3.6. Isotopes as hydrological tracers

The stable isotopic composition of meteoric-derived water is sensitive so a variety of environmental conditions, including temperature, altitude, continentality and evaporation. Because of this, the ratios of stable isotopes of hydrogen and oxygen are useful tracers of hydrological processes and conditions. Stable isotopes are atoms of specific elements that are defined by the number of neotrons and protons in the nucleus. For example, a carbon atom usually has 6 protons and 6 neutrons in its nucleus (i.e. ^{12}C), however, a small proportion of carbon atoms have an extra neutron (i.e. ^{13}C). This extra mass subtly changes how molecules with ^{13}C behave in the environment in a process known as fractionation. These differences in behaviour can be useful in tracing and studying natural processes.

Fractionation occurs due to the mass differences between molecules that are composed different stable isotopes. The isotopic composition, or relative abundance of heavy and light isotopes, of a substance changes as a result of condensation, evaporation, freezing, melting, chemical reactions, and biological processes (Freeze & Cherry, 1979). There are two types of fractionation, known as kinetic fractionation and equilibrium fractionation. Kinetic fractionation occurs through certain irreversible processes in nature such as evaporation and condensation. ^{2}H and ^{18}O containing water molecules, for example, vibrate faster and tend to evaporate more readily, while ^{1}H and ^{16}O containing water molecules tend to condense more readily. Fractionation also occurs through irreversible processes such as photosynthesis in which case a product depleted in ^{13}C will gradually accumulate (Cook & Herczeg, 2000). Equilibrium fractionation occurs due to the chemical bonds of lighter isotopes being slightly weaker. The same kind of bonds are formed between light and heavy isotopes, however, heavier isotopes form stronger bonds due to their greater mass. Bonds formed by light isotopes are more readily broken, therefore these lighter molecules react more quickly during reversible reactions or phase changes (Stumm & Morgan, 1996). As a result of this the product of the reaction will be more readily composed of lighter isotopes.

Isotopic data is measured against standards and are recorded as delta:

$$\delta^{13}\mathrm{C} = \left(\frac{\left(\frac{^{13}\mathrm{C}}{^{12}\mathrm{C}}\right)_{\mathbf{sample}}}{\left(\frac{^{13}\mathrm{C}}{^{12}\mathrm{C}}\right)_{\mathbf{standard}}} - 1 \right) * 1000\ {}^{o}/_{oo}$$

For example, a sample with a $d^{13}C$ of -15‰ indicates that the sample is depleted in ^{13}C relative to the standard by 15‰. Worldwide standards are used to compare stable carbon isotope ratios against. Oxygen and hydrogen isotopes are compared to the isotopic ratio of standard mean ocean water (SMOW). Stable carbon isotope samples are compared to the isotopic composition of Pee Dee Belemnite (PBD), which is a marine fossil found from the Pee Dee geological formation is South Carolina. For example, Pee Dee Belemnite is defined as having a $\delta^{13}C$ of 0 ‰.

Stable hydrogen and oxygen isotopes

The isotopes of oxygen and hydrogen are particularly useful for tracing hydrological processes. Ocean water contains a certain proportion of ^{18}O and ^{2}H which varies in a predictable manner and can be plotted against one another where they correlate along what is known as the Global Meteoric Water Line (GMWL) (Figure 1-4). This has been calculated from compiling the isotopic composition of waters from all over the world and plotting their *respective* $\delta^{2}H$ and $\delta^{18}O$ *against* one another.

The relationship is described by the following equation:

$$\delta^2H = 8\,\delta^{18}O+10$$

Where a particular body of water will fall along this line will vary with regional, latitudinal, altitude and climatic differences. Specific sets of data will fall slightly differently depending on local conditions. For example, cooler climates have precipitation that is more isotopically depleted thus sits lower on the meteoric water line. The same is true of precipitation in higher altitudes and areas further inland. As ocean water under fractionation it becomes depleted in the heavier isotopes of oxygen and hydrogen and is reflected in the y-intercept of 10 on the GMWL, which is a function of the approximately 10‰ enrichment in deuterium of vapour which has evaporated from the ocean (Kendall & McDonnell, 1998). This is also known as the deuterium excess. As a guideline for New Zealand it has been established that for every 100 metre gain in altitude there will be a -0.23‰ enrichment of $\delta^{18}O$ *and a -1.80‰ enrichment of* δ^2H (Stewart & Taylor, 1981).

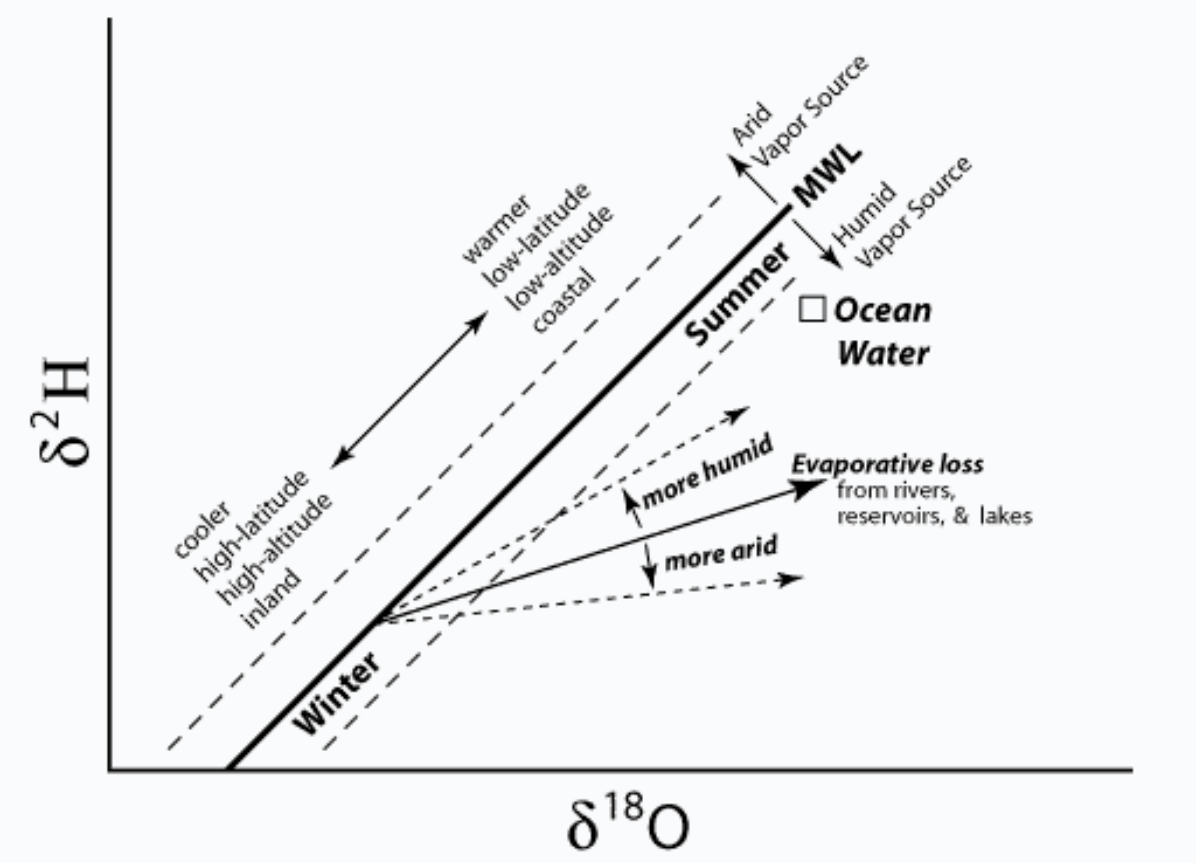

Figure 1-4 δ2H Vs. δ18O and the global meteoric waterline *(GMWL) with the effects of different climates, altitudes and latitudes displayed (SAHRA, 2016)*. Water samples globally will tend to plot along the GMWL.

This phenomenon can be used to track and study hydrological processes. For example, water in a given stream that originates in the head waters of a valley will often have a different isotopic composition to water that has fallen further down the catchment. This has been used for example to show that the water supply for Christchurch city, which is derived from groundwater directly below the city, originates predominantly from the Waimakariri River, an alpine river, rather than water that falls closer to the coast on the Canterbury plains. Water from the Waimakariri is depleted in ^{18}O relative to water that falls on the plains and this depleted ^{18}O composition corresponds to that which lies in aquifers under Christchurch city (Rosen, 2001).

Evaporative loss from rivers, reservoirs and lakes will push the isotopic composition of water off of the GMWL towards a greater proportion of ^{18}O. This is because water molecules containing just ^{2}H will evaporate more readily than those that contain ^{18}O, leading to a reduction in the deuterium excess in evaporated water. The extent of this drop in deuterium excess can be used as a measure of relative levels of evaporation occurring between different samples.

Stable Carbon isotopes

The stable isotopes of carbon are particularly useful at tracing the interaction of water with the soil zone and carbonate minerals, and hence for tracing the connectivity of groundwater to surface water. The isotopic evolution of DIC (DIC) begins with the dissolution of atmospheric CO_2 (-8‰) by meteoric water. During photosynthesis plants discriminate against ^{13}C in favour of ^{12}C, leading to a depletion of ^{13}C in organic plant matter (-23‰). This happens in two steps. First of all there is a preferential uptake of ^{12}C from the atmosphere by plants. This is then followed by a preferential conversion of ^{12}C enriched dissolved CO_2 to phosphoglyceric acid, which is the first product of photosynthesis (Stumm & Morgan, 1996). The actual isotopic composition of soil derived CO_2 depends on the photosynthetic pathway of the vegetation that dominates the surface. The C_3 pathway dominates in 85% of terrestrial plants and gives $\delta^{13}C$ values in the range from -24 to -30‰ V-PDB (Gray, 2011). This photosynthetically derived organic matter accumulates in the soil where aerobic bacteria convert the majority back to CO_2. This results in soil concentrations 10-100 times greater than that in the atmosphere (Gray, 2011). These isotopic shifts can be used for example to aid in the identification of the source and flow path of water in a stream as groundwater derived flow should show a relative depletion in ^{13}C (Figure 1-5).

The value DIC in soil water and in groundwater will reflect the mixing of both soil CO_2 from photosynthesis and subsequent microbial respiration, and carbonate mineral dissolution. Carbonate minerals have been found to have a of approximately 0‰ V-PDB (Taylor & Fox, 1996). Groundwater will thus reflect the relative mixing of soil derived carbon and that derived from carbonate weathering. If the of soil is taken as -22‰, then the DIC present in groundwater derived solely from the carbonic acid weathering of calcite will have a -DIC value of -12‰ assuming that equilibrium has been met, i.e. half of the DIC present comes from calcite and the other half from dissolved DIC from the soil zone (Doctor et al., 2008). Thus the of groundwater will reflect the extent to which calcite weathering has occurred.

From the point of seepage of groundwater into a stream and some distance downstream there can be a rapid increase is due to outgassing. This is where DIC in-streams is lost to the atmosphere resulting in the gradual accumulation of enrichment of 13C-DIC in the remaining water. Thus a stream will show a gradual increase in value downstream of any groundwater inputs. Another interpretation of this is that high levels of photosynthetic activity of aquatic plants enriches the remaining water in ^{13}C (Doctor et al., 2008).

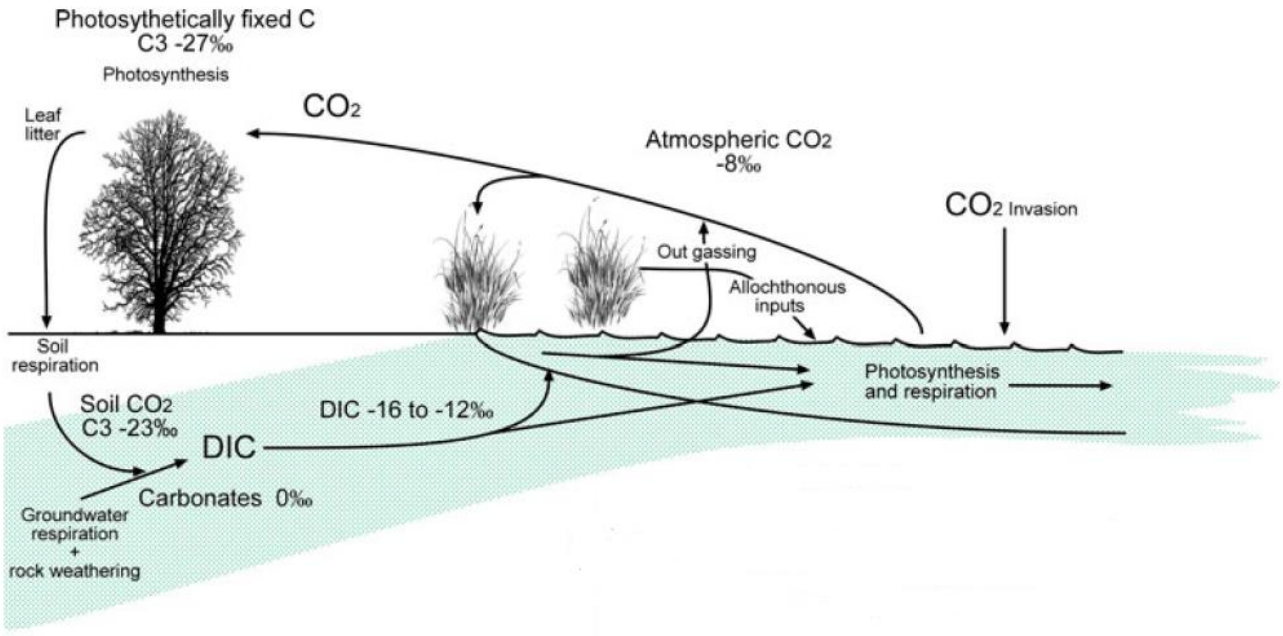

Figure 1-5 Isotpoic fractionation of carbon. This conceptual diagram displays the different pathways and forms of carbon that influence the isotopic composition of surface waters (Gray, 2011).

1.4. Waimea Stream current state

The Waimea Stream is an inland stream in Southland. It drains the Lintley ranges before travelling several kilometres across the Waimea plains and discharging into the Mataura River, a major Southland river that drains the Eyre Mountains to the north (Figure 1-6). The Waimea Stream has been identified as having some of the highest nitrate concentrations in the Mataura catchment as far back as the early 1980's. Indeed, it is thought that the Waimea Stream may be having a negative impact on the water quality of the Mataura River itself (Riddell, 1984). The Waimea stream is suspected of having significant gains from groundwater high in nitrate which is contributing to the high in-stream nitrate concentrations (K. Wilson, 2010). Observations have been made that indicate an overall decline in-stream health with elevated periphyton and macrophyte levels as well as lower fish numbers, although no quantitative monitoring of periphyton and macrophyte levels have been done for the Waimea Stream along its length. Elevated nutrient levels can promote the growth of nuisance periphyton and macrophyte which can negatively impact the ecology of a stream (Biggs, 2000b). A survey undertaken of the Waimea Stream at Mandeville in August of 2008 as part of Environment Southland's State of the Environment monitoring obligations, found limited fish numbers, despite expectations of a more diverse and abundant fish community (Ledington, 2008).

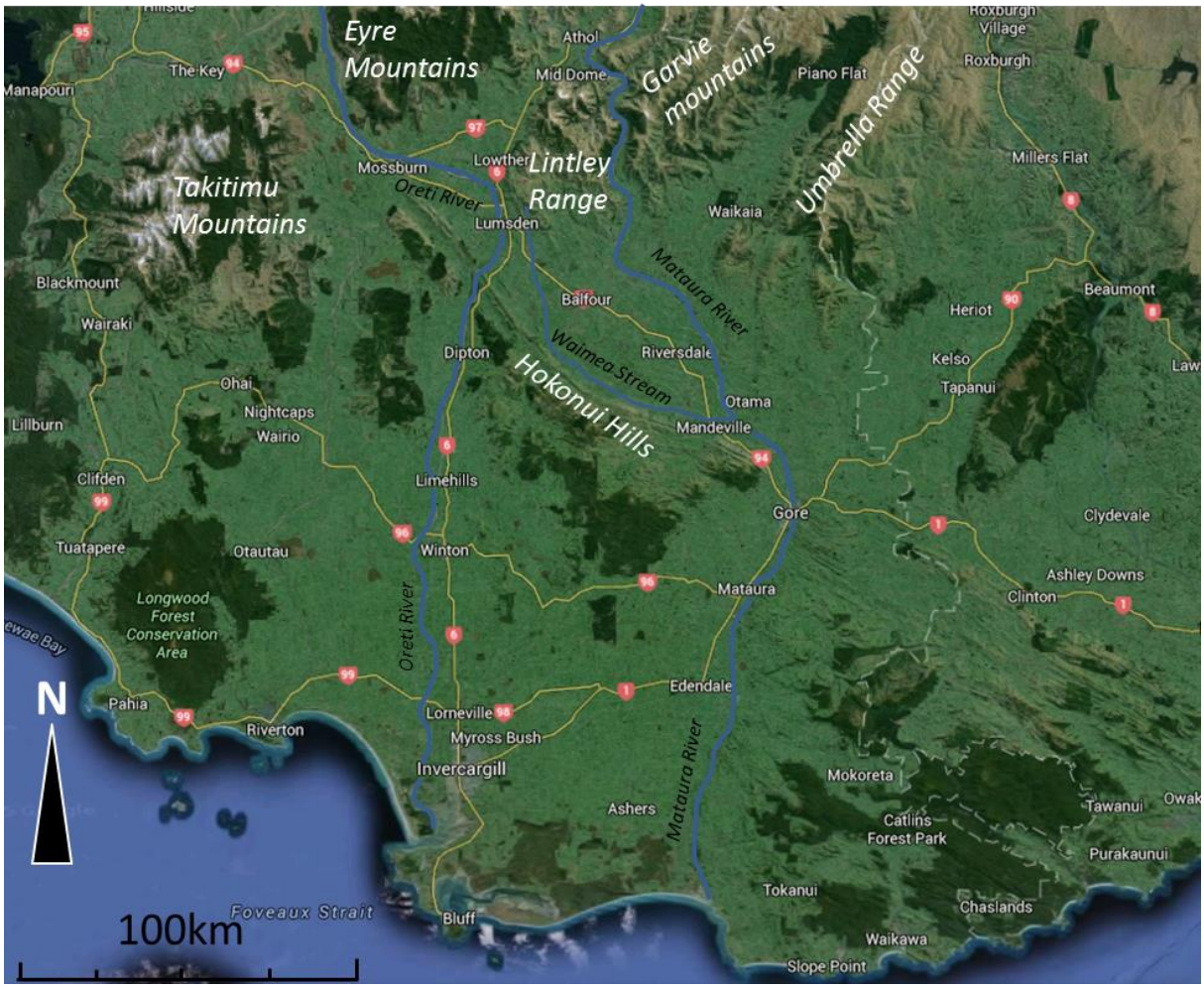

Figure 1-6 Map of Southland with the Waimea Stream, Oreti River and Matarua Rivers displayed (blue lines).

The soils of low lying areas such as the Waimea plains are typically poorly drained as a result of high clay content coupled with the relatively flat topography (Rissmann et al., 2016a). In response to this there has been wide spread development of artificial drain networks, both mole tile and surface drains. This has dramatically altered the natural hydrology of the area. The Waimea Stream has also lost many kilometres of stream length due to extensive channel straightening. Historically, excess rainfall would have been stored in extensive wetlands as well as in ground water which would then be slowly released during dry periods over summer (Figure 1-7). However, as a result of artificial drainage, excess rain flows much more rapidly through, and is discharged from, the catchment (K. Wilson, 2010). As a consequence of this much less water is available to be slowly released during dry periods, thus leading to reduced summer surface flows (K. Wilson, 2010).

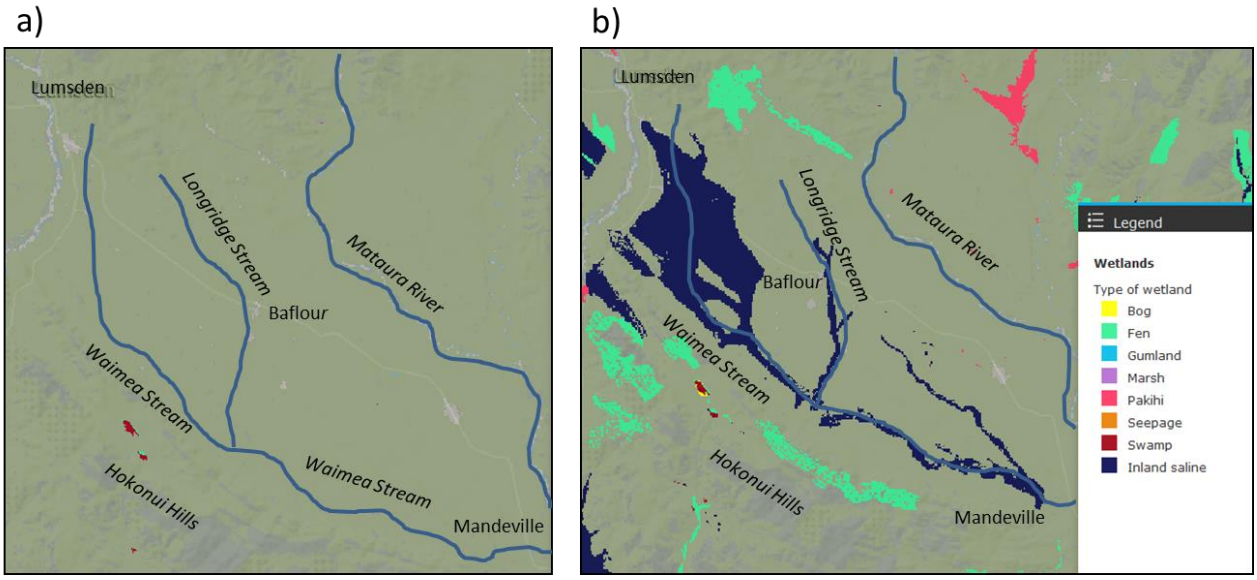

Figure 1-7 Wetland cover on the Waimea Plains in a) 2008 and b) pre-human. See key for type of wetland cover (Statsnz, 2016).

The Waimea stream is suspected of being hydrologically connected to the Waimea plains aquifer which has shown increasingly high levels of nitrate (B. N. Hughes, 2008; Rissmann, 2012; K. Wilson, 2010), although the dynamic and the extent of the connection is poorly understood. A stream that is spring fed will typically reflect the water quality of the groundwater that feeds it, hence it is important to gain a greater understanding of the hydrological connection between the Waimea Stream and area's groundwater. It is unclear whether the deteriorating surface water quality of the Waimea Stream is a function of groundwater high in nitrate, or a function of overland flow inputs, or a combination of the two.

An area on the Waimea plains near Balfour has very high groundwater nitrate concentrations ranging up to 20 mg/L (NO_3-N) in some places (B. N. Hughes, 2008; Rissmann, 2012; K. Wilson, 2010). This area is known as the 'Balfour nitrate hotspot' (Figure 1-8). Groundwater nitrate concentrations around Balfour have been gradually increasing over the past decade and a half. A bore near the Balfour nitrate hotspot (E44/0047), from 2005 to 2012, showed an average increase in nitrate of 0.9 mg/L per year (K. Wilson, 2010). Regular monthly sampling of the Waimea Stream has shown that nitrate concentrations increase markedly from the headwaters near Lumsden through to where the Waimea Stream meets the Mataura River. A large proportion of this increase in nitrate concentration coincides geographically with the Balfour nitrate hotspot. This, along with the fact that nitrate concentrations remain elevated during summer in the Waimea Stream down gradient of the Balfour nitrate hotspot, suggests that groundwater may possibly be contributing significantly to in-stream nitrate concentrations (Figure 1-8).

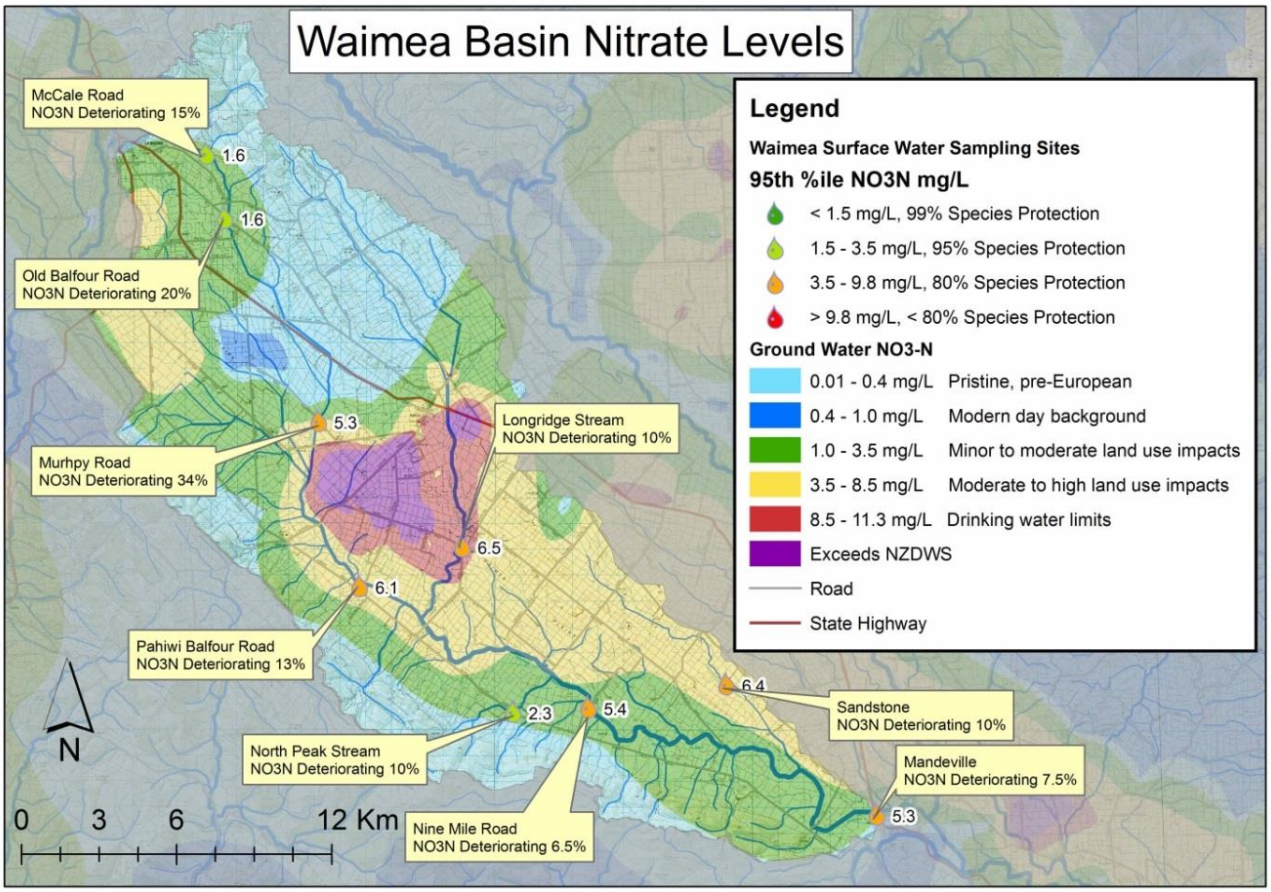

Figure 1-8 Map of the of the Waimea plains groundwater nitrate (NO_3-N) concentrations with median nitrate concentrations are displayed for the Waimea Stream, Longridge Stream, North Peak Stream and Sandstone Stream. This map has been produced by Environment Southland (R. Hudson, personal communication, November 21 2015).

1.4.1. Hydrology of the Waimea catchment

The Waimea Stream is a low relief stream in Southland, New Zealand, with a catchment area of approximately 400Km^2. The stream drops roughly 100 metres from the furthest upstream site monitored at Old Balfour Road to where it joins the Matarua River near Mandeville. From where it exits the Lintley Range as a small stream it is at an elevation of approximately 200 metres above sea level. It then slowly drops to 100 metres above sea level at the point where it joins the Mataura River. The Waimea stream has its headwaters ultimately in the Lintley Range (approximately 400-600m elevation) which lies to the North of the Waimea Plains, however this is a small fraction of the total catchment, making up less than 20km^2 of the total. The Waimea Stream is also fed by Longridge Stream which runs along the north east side of Longridge before crossing the Waimea Plains and joining the Waimea Stream near Sandstone. Another significant low lying tributary is Sandstone Stream which enters the Waimea Stream approximately 8 km above the Mataura confluence. The Waimea Plains are bounded on their south western side by the Hokonui Hills and by the Longridge terraces to the north east. The Oreti River, a large Southland River that is alpine in origin, runs north to south directly west of the Waimea Plains, with little relief seperating the two.

A flood channel of the Oreti river and associated gravel deposits have been identified as running across the Waimea plains in line with where the mid to lower Waimea Stream currently runs. Research has suggested that during Otiran glaciation, when river levels were much greater, a flood channel of the Oreti ran across the Waimea Plains from just south of Lumsden to the Waimea Stream and along to Mandeville (Figure 1-9). This has led to speculation of a possible hydrological

connection between the Oreti river, the Waimea Plains aquifer, and the Waimea Stream itself (Mcintosh, Carrick, & Lauren, 1998).

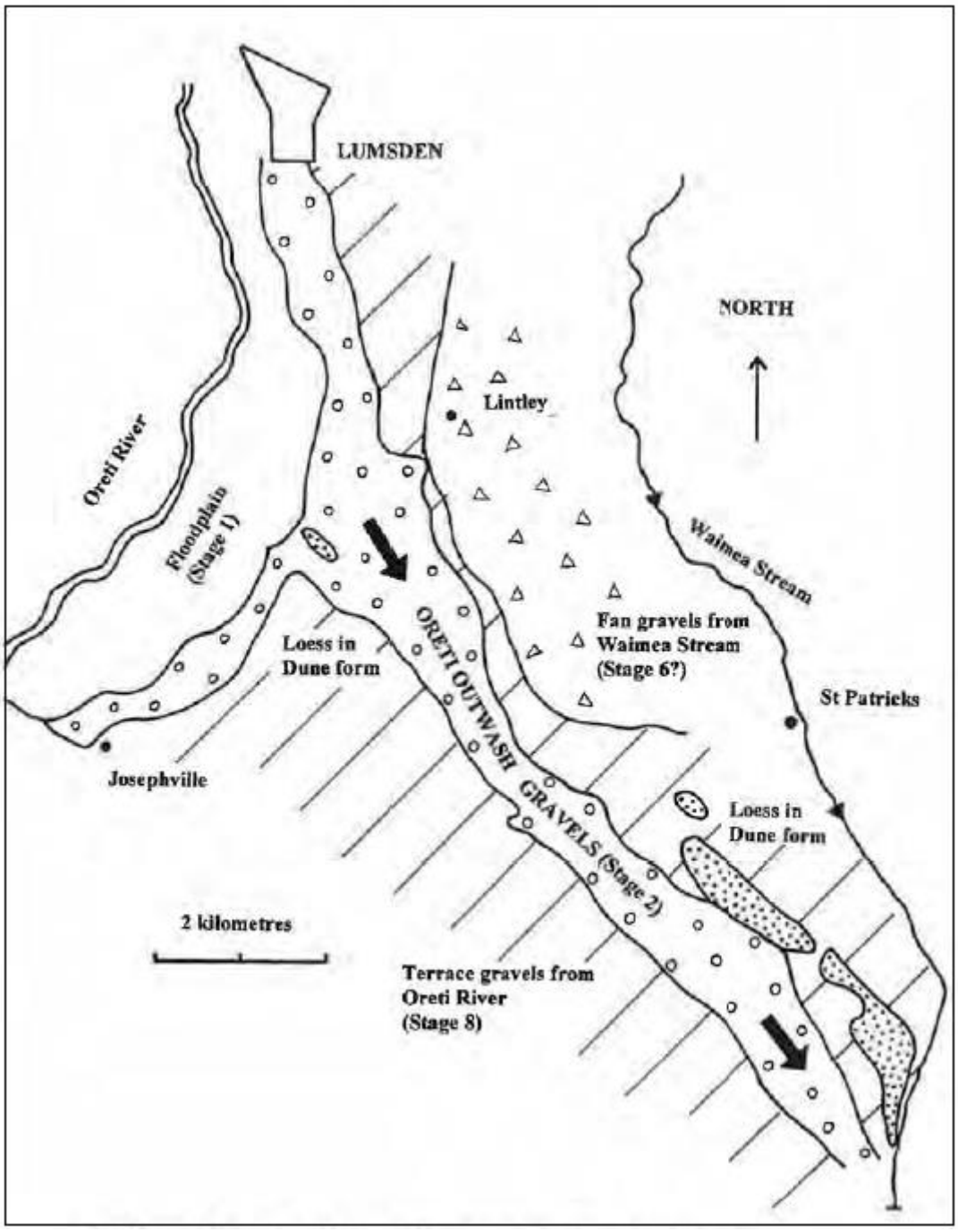

Figure 1-9 Waimea Plains Otiran flood channel sketch map of the area south of Lumsden, showing the Otiran flood channel (Mcintosh et al., 1998).

The Waimea Stream is a moderately sized river with an historical mean flow of 3.598 m^3/s (Environment Southland, 2016). Flow recording at Mandeville indicates that flows are relatively stable, although extremes at both ends of the scale do occur, with the lowest recorded flow at this site being 0.107 m^3/s, while there is also the capacity for the stream to carry well over 100 times its mean annual flow during floods (Table 1-2). The Waimea stream tends to see lower flows over the summer months, with its lowest flows generally occurring during February and March, before rising

to a peak during the winter months of June and July, after which levels gradually decrease to their summer levels (Figure 1-10).

Table 1-2 Summary of the Waimea Stream hydrology. Historical flow data for the Waimea Stream at Mandeville. Data has been obtained from Environment Southland (Environment Southland, 2016).

	Flow ($m^{3/}$sec)
Mean Flow	3.598
Median Flow	1.474
Highest Recorded Flow	244
Mean annual Flood	76
Lowest Recorded Flow	0.107
7 Day Mean Annual Low Flow	0.358

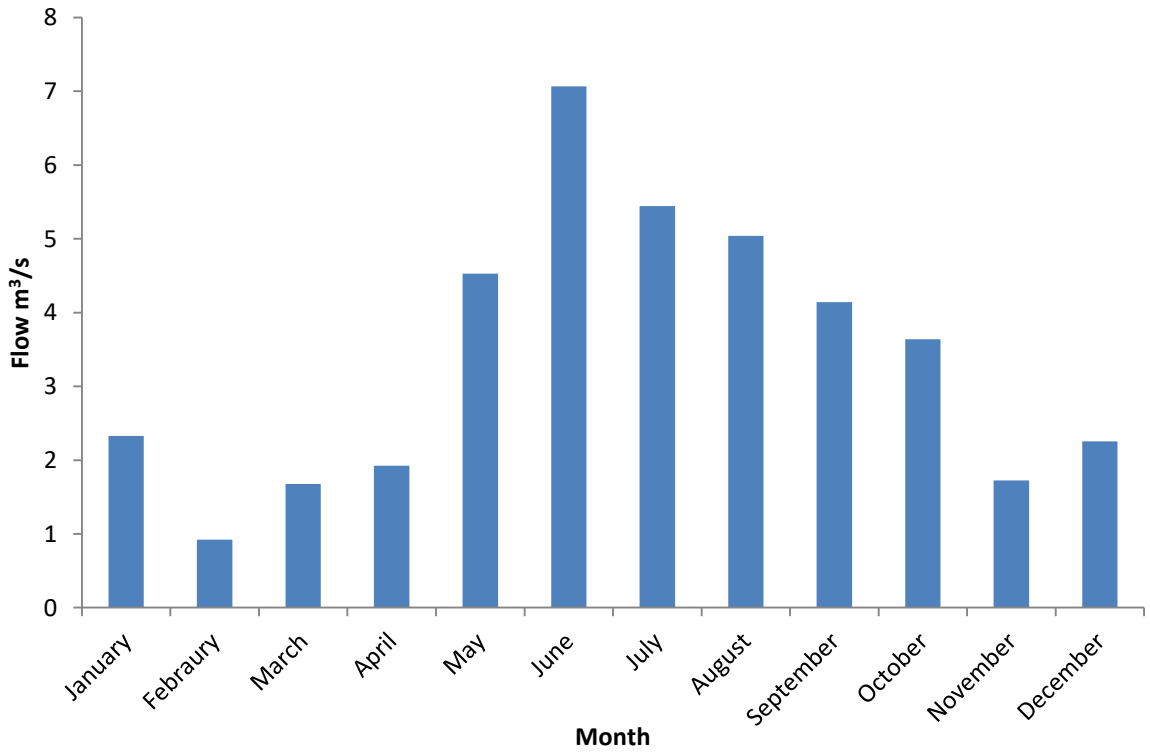

Figure 1-10 Waimea Stream mean monthly flow at Mandeville for the period 2004-2015. Flow data has been obtained from Environment Southland (D, May, personal communication, 15th December 2015).

There is thought to be a connection between the Waimea Plains groundwater and the Waimea Stream, although the extent and dynamics of this connection have not been fully elucidated. A study investigating concurrent flow rates on the Waimea during October 2009 found that the Waimea and Longridge streams both experienced gains in flows that were larger than what could be accounted for by tributary inputs (K. Wilson, 2010). It was concluded from this that these reaches were most likely gaining flow from groundwater, and that the greatest gains were seen in the area nearest the Waimea-Longridge confluence (Figure 1-11). Significantly, this corresponds to the area of highly elevated groundwater nitrate near Balfour.

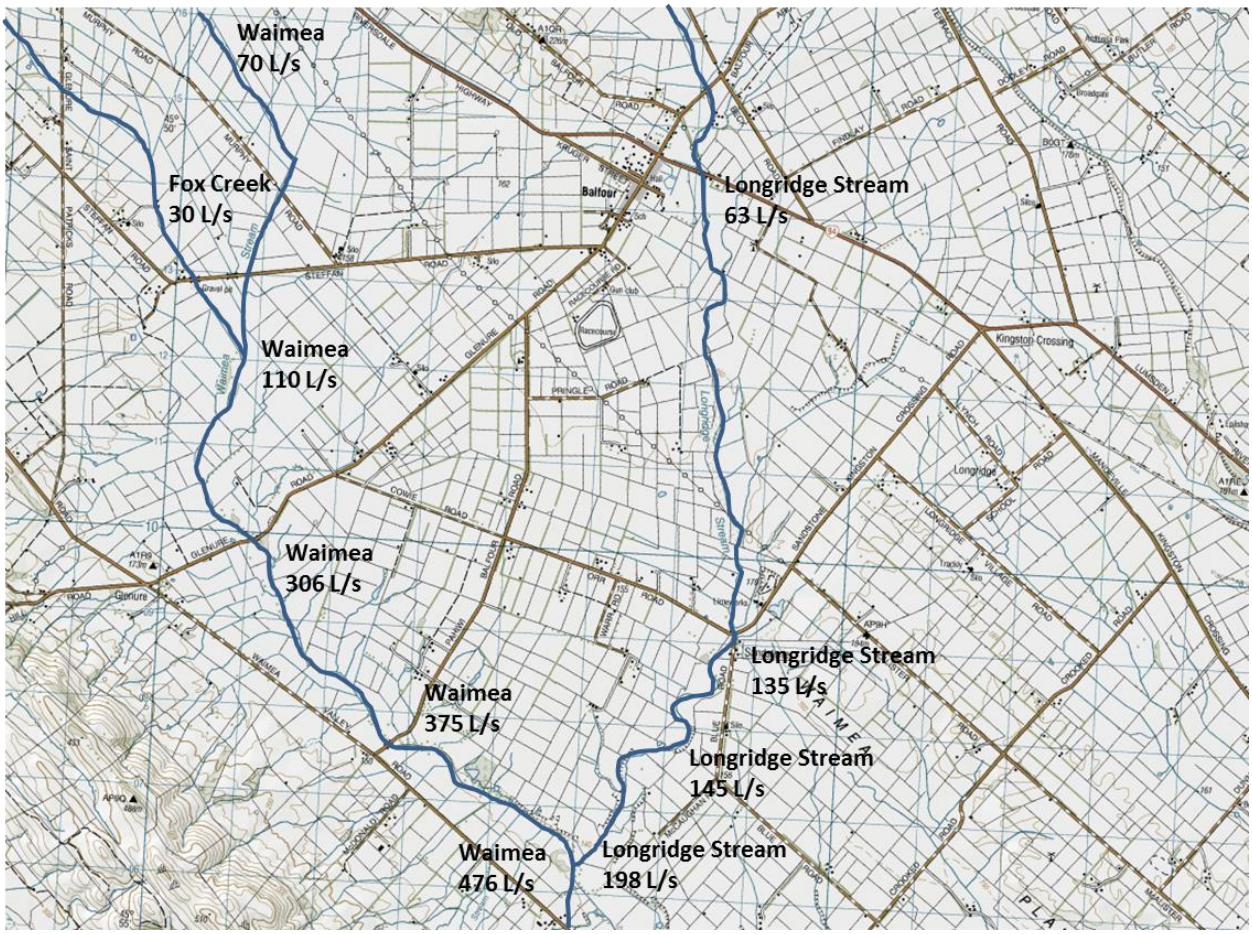

Figure 1-11 Concurrent flow gauging of the Waimea and Longridge streams undertaken during October 2009 (K. Wilson, 2010). Flow is displayed in litres/second.

1.4.2. Southland's aquifers

Southland's aquifers are lie within a relatively thin (20-70m) veneer of alluvial sediments that are spread across a deeper layer of extensive marine sediment and lignite sequences (K. Wilson, 2010). These alluvial sediments were lain down over periods of glacial advance and retreat during the Quaternary period (2 million years ago). Subsequent reworking of these gravel deposits by major river systems, which were much larger than exist today in the area, has resulted in a series of broad terraces flanked by flood plains (Turnbull & Allibone, 2003).

The aquifers of the Southland region have been identified as having a heightened risk of groundwater contamination, with approximately 85% of Southland aquifers showing a high level of sensitivity to contamination (Rissmann, 2012). Two factors contribute to the sensitivity of Southland's aquifers to nitrate contamination. The first is that the aquifers are generally unconfined. An unconfined aquifer, as opposed to a confined one, lacks a layer of relatively impermeable soils, such as marine sediments, that separates the groundwater from the surface. In an unconfined aquifer, water, along with other water soluble contaminants such as nitrates, can percolates through the soil surface and readily find their way down into the groundwater.

Secondly, the alluvial sediments that compose Southland's aquifers are in places relatively poor in organic material. This has important consequences for the level of bacterial denitrification that can occur (Rissmann, 2011; Rissmann et al., 2016a). Denitrification potential however does vary regionally with markedly different levels of denitrification possible within relatively small areas. For example, the Waimea Plains have areas where there are relatively low levels of denitrification

potential as well as areas with relatively high levels of denitrification potential. Denitrification relies on bacteria which utilise nitrates in order to oxidise organic matter, allowing them to release the energy stored in the organic matter (Freeze & Cherry, 1979). These bacteria reduce nitrate to nitrogen gas which is then released from the ground. Areas of low denitrification potential are susceptible to accumulating nitrate in groundwater. If oxygen is present, microorganisms will preferentially utilise oxygen over nitrate, thus in terms of denitrification potential the level of organic content is important as well as the local redox state, i.e., whether the soil zone is oxic or anoxic.

Across the Southland region, within the Ground Water Management Zone (GWMZ), which excludes conservation areas such as Fiordland National Park, there have been widespread increases in groundwater nitrate concentrations (Rissmann, 2012). As a point of comparison, a "pre-European" concentration of NO_3-N of 0.4mg/L has been determined by assessing the nitrate concentration for shallow oxidising groundwater beneath old growth indigenous forests below Fiordland, other areas of the Southland conservation estate, and on Stewart Island. Approximately half of the GWMZ shows some impact from human activities, i.e. nitrate concentrations greater than 1.0 mg/L (Rissmann, 2012). Testing based on 58 testing sites across Southland from 1995-2008 revealed that 36% of the bores showed an increasing trend in nitrate concentrations (Te Ao Marama, 2010). Groundwater nitrate contamination is not uniform across the region however, with very high levels occurring in several 'hotspots', relatively defined areas of particularly high groundwater nitrate (Figure 1-12). Across Southland, 2% of the GWMZ has nitrate concentrations above 8.5mg/L, while 0.8% exceeds the maximum allowable value (MAV) for drinking water of 11.3mg/L. A further 19% have nitrate concentrations ranging from 3.5-8.5mg/L, while 27% have nitrate concentrations ranging from 1.0-3.5mg/L (Rissmann, 2012).

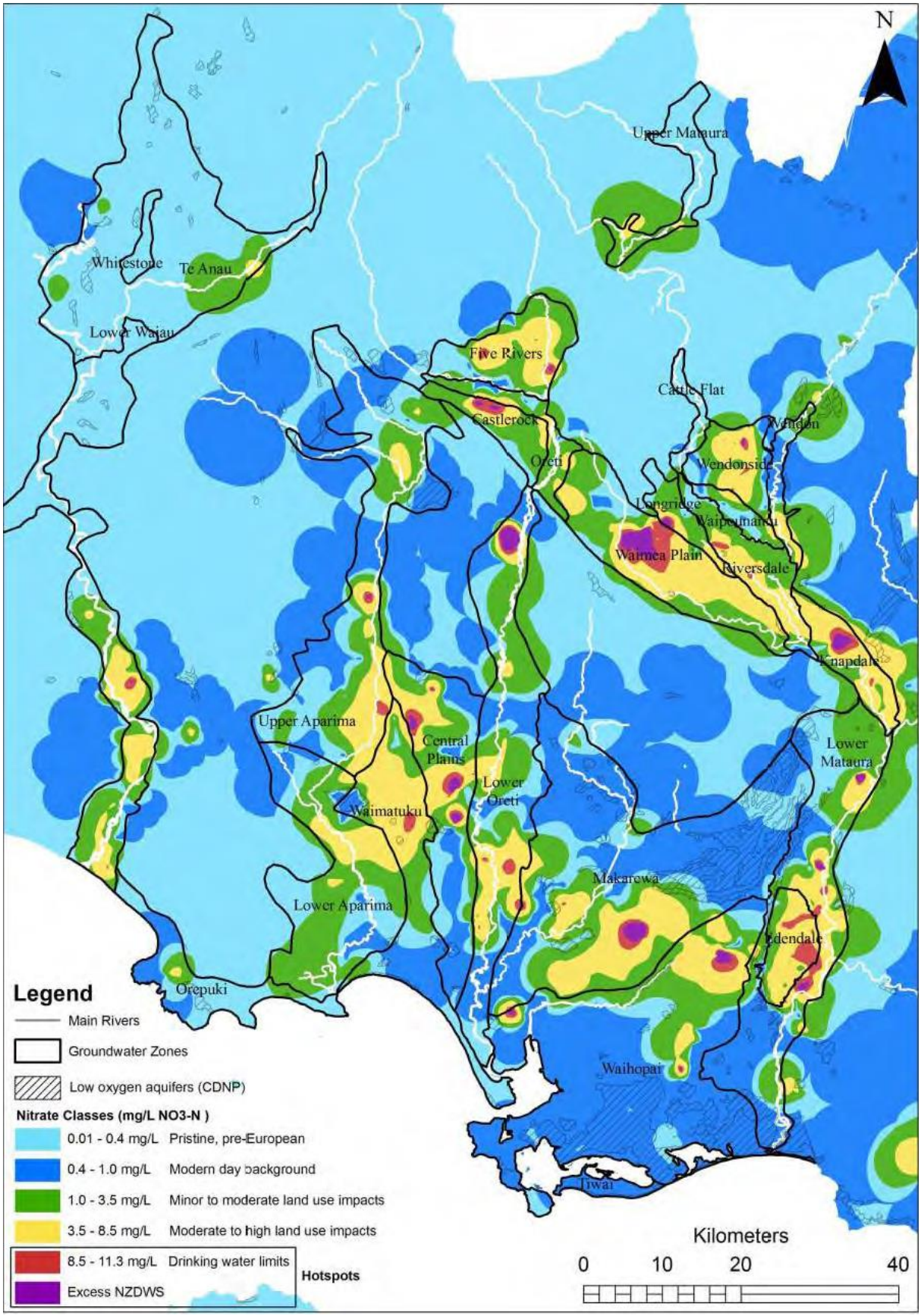

Figure 1-12 Map of Southland's major aquifers and areas of elevated groundwater nitrate. The major groundwater zones (black lines, names in black text), main stem rivers, low oxygen aquifers, along with ground water nitrate concentrations are displayed (see key) (Rissmann, 2012).

1.4.3. Waimea Plains climate

The climate of Southland is dominated by the influence of prevailing west to south-west winds which transport moisture laden air from the Tasman Sea. This creates a large rainfall gradient across the region. These winds are intercepted by the mountains of Fiordland, which line the western coastline, and the foothills of the Southland plains, creating a rain shadow that leaves inland basins, such as the Waimea Plains relatively dry. The Waimea basin receives on average annual precipitation of 750mm, this compares to between 1000mm and 1250mm along the south coast, and to between 4000mm and 7500mm along the mountainous Fiordland coast to the west (Ledgard, 2013). Dry north-westerly weather which predominates over the summer months increases levels of evapotranspiration, which can, when severe or prolonged, result in significant soil moisture deficits on the Waimea Plains. Conversely, precipitation over the winter is not significantly greater than that of the summer months, yet conditions are much wetter due to very low levels of evapotranspiration (Figure 1-13).

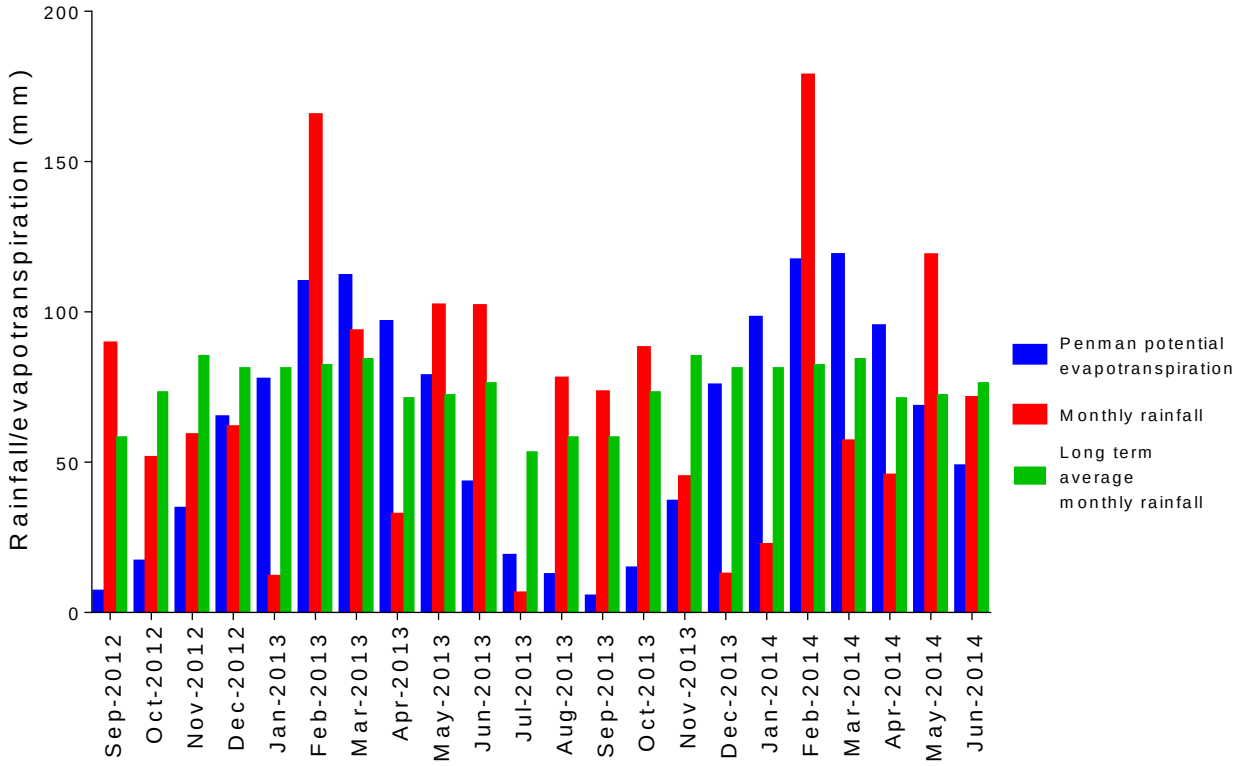

Figure 1-13 Waimea Plains rainfall and Penman potential evapotranspiration from September 2012 to June 2014. Monthly accumulated rainfall and Penman evapotranspiration (d) data has been obtained from NIWA (Riverdale, York Road (station number: 38645. Latitude: -45.904, longitude: 168.739) (NIWA, 2016), while average monthly rainfall has been obtained from Environment Southland (Environment Southland, 2016).

1.4.4. Waimea Plains geology and hydrogeology

Data collected from a number of drillers logs has shown that to the southeast of the Waimea Stream the basement rocks (mudstone) underlie a claybound gravel layer that is approximately 15 m thick, while to the north west the basement rocks are located about 35 m deep and the overlaying gravels have more clearly defined layers of up to 10 m thick (K. Wilson, 2010). To the northeast the basement rocks under the Longridge terrace are far shallower than on the flood plain. The increase

in land elevation due to the deposition of sediments, or aggradation, between the older gravels of the Longridge terrace and the relatively younger gravels of the Waimea Plains extends south of Steffen Road. This indicates that there is an indistinct yet wide boundary between the Longridge and Waimea Plains groundwater zones (K. Wilson, 2010).

The fluvial deposits on the Waimea Plains have varying degrees of age and weathering, with quaternary 2, 4 and 6 deposits. The Lintley Range in which the Waimea Stream has its headwaters is comprised principally of Haast Schist of the Caples terrane. To the south, the Hokonui Hills are comprised of sandstone and siltstone of the Murihiku and Dun Mountain-Maitai terrane (Turnbull & Allibone, 2003).

Pump testing has been carried out in the area to determine the average bulk seepage velocity. This has been calculated based on an average saturated thickness of 10 metres determined from bore log data, an aquifer transmissitivity of 300 m^2/day, an hydraulic gradient of 0.004, and an assumed porosity of 0.25 which gave an average bulk seepage velocity through the aquifer of 175 m/year (B. N. Hughes, 2008). This slow rate of groundwater movement makes the groundwater vulnerable to cumulative land use impacts as it takes a long time for any contaminants entering the groundwater to move through the system (K. Wilson, 2010). Velocity rates are however likely to vary across the plains due to the levels of heterogeneity. Nevertheless, this is still indicative of a relatively slow bulk movement of groundwater.

A slow rate of groundwater movement can manifest itself as a contamination legacy scenario, whereby changes due to shifts in lad use on the surface take a long time to move through the system. A consequence of this can be that contaminated groundwater may impact surface water flows well into the future, despite a subsequent shift to lower inputs of nitrates from surface land use. Work carried out to estimate the average travel time for water and nitrates across Southland to percolate through the unsaturated zone has indicated that for 80% of Southland it takes less than 5 years, while for 90% it takes only two years (S. Wilson, Pierre, Rissman, & Ledgard, 2014). This suggests that a shift in land practices on the surface could lead to a decrease in additional nitrates entering the groundwater within a relatively short time period (i.e. 2-5 years). However, although a reduction in additional nitrates entering the groundwater system can be achieved in a relatively short period, nitrate already present in the groundwater may take a significant amount of time to actually move through and be flushed from the groundwater system itself.

The topology and geography of an area strongly influences the flow of groundwater. The Balfour area has a relatively complex groundwater flow. North of the Dipton-Balfour road the direction of flow is in an overall south-easterly direction with a reasonably flat hydraulic gradient of 0.002. To the south of the Dipton-Balfour road the groundwater flow is in an overall southerly direction, towards the confluence of the Longridge and Wiamea streams the hydraulic gradient is much steeper at 0.011 (K. Wilson, 2010). Piezometric surveying data has pointed to the area to the southeast of the Dipton-Balfour road along to the confluence of the Waimea and Longridge Streams as being an aquifer discharge area (Figure 1-14).

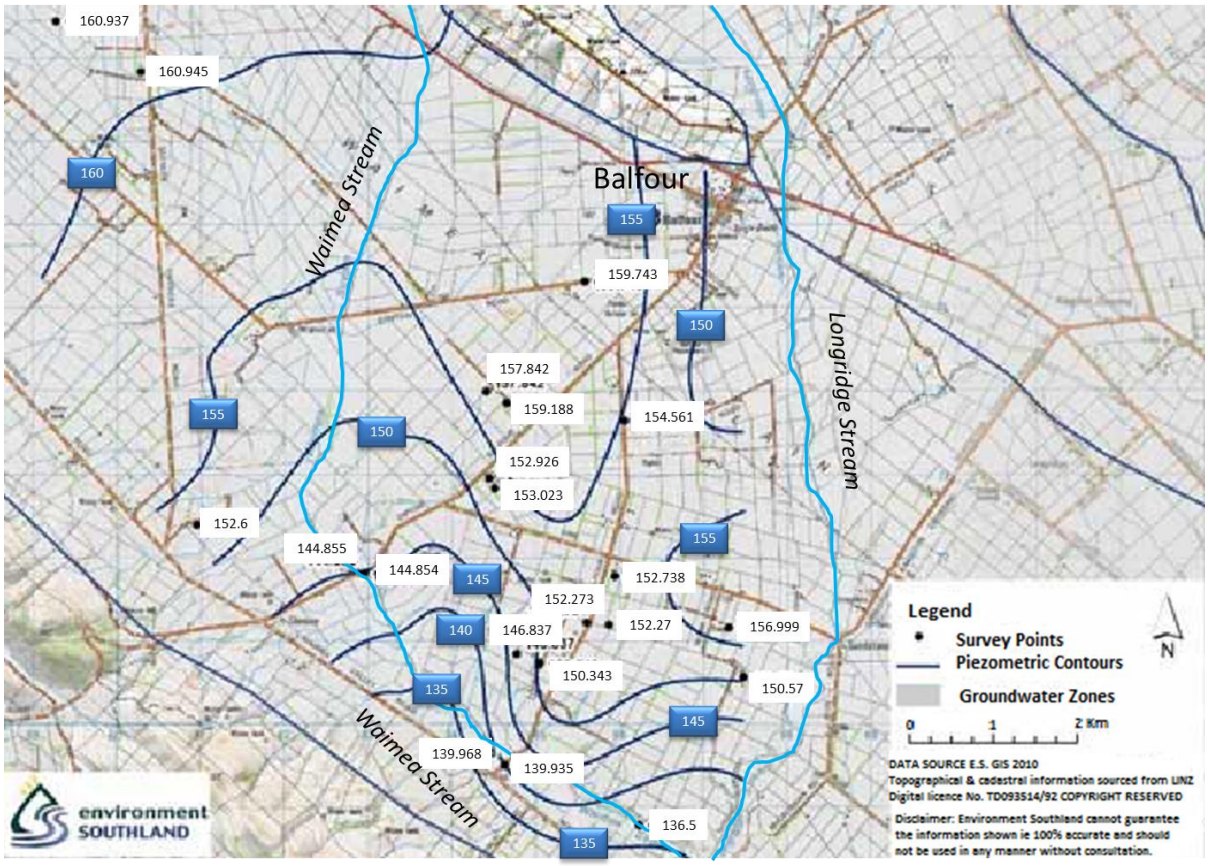

Figure 1-14 Map of groundwater flow on the Waimea Plains from piezometric surveying data (collected 9-11th February 2011) (K. Wilson, 2010). See figure for key.

Groundwater levels show some variation throughout the year with an overall trend of higher groundwater levels during winter and spring, which progressively declines over summer and autumn before being recharged over the winter months. These levels fluctuate annually between 1-2 metres in the Waimea area, while bores on the Longridge groundwater zone exhibit fluctuations between 1-4 metres (K. Wilson, 2010).

1.4.5. Waimea Plains physiographics

It has been observed that across Southland similar farming operations can result in markedly different outcomes in terms of hydrochemistry and water quality. Such differences appear to even occur within geographically quite small areas, for example either side of a river or indeed a fence line. The 'Balfour nitrate hotspot' on the Waimea Plains is an example of this, where similar farming practices across the plains have led to dramatically different outcomes in terms of ground water nitrate concentrations. In order to better understand differences in regional water quality and chemistry, Environment Southland has produced a physiographic map of the Southland region (Rissmann et al., 2016a). This is a map of regional differences in a number of factors such as geology, topology, and climate which influence regional differences in hydrochemistry. The map acts as a predictor of regional differences in hydrochemistry by looking at and mapping four key drivers of hydrochemistry:

- precipitation source
- recharge mechanism and water source
- combined soil and geological reduction potential
- a combination of geomorphic setting and substrate (rock or biological sediment) composition

Precipitation source shows two key trends, a decrease of marine aerosols as one moves inland and towards higher elevations within Southland, as well as a trend towards depleted $\delta^{18}O\text{-}H_2O$. This is a result of Na and Cl being rained out as the cloud mass moves inland. The same applies to $\delta^{18}O\text{-}H_2O$ where fractionation occurs due the preferential precipitation of the heavier stable oxygen isotope as the cloud mass moves inland and towards greater elevations. The precipitation of Southland reflects the chemical composition of sea water with Na-Cl dominating the solute content with $Na>Cl>Mg>SO_4$. K and Ca make up less than 5% of the solutes in Southland rainfall (Rissmann et al., 2016b). It has been found that surface waters across the region generally reflect the influence of marine aerosols, with a slight enrichment of sodium, which is thought to be the result of water rock interactions (Rissmann et al., 2016b).

The Waimea Plains have high levels of fast artificial by pass flow due to an extensive network of artificial drainage. The area around Balfour that aligns with the 'Balfour nitrate hotspot' has low levels of artificial drainage as the soils themselves are naturally well drained. Local recharge can for example be via rapid overland flow in-streams via artificial drainage system which tend to exist on poorly drained soils, or through direct percolation horizontally through the unsaturated zone into well drained soils. In the former case the hydrochemistry of a stream running through the an area subject to rapid overland flow events will tend to see spikes in solutes related to high rainfall events

A key driver of differences in soil chemistry across Southland is the degree of age and weathering of the soil. This makes up approximately 65% of regional variation. Geological age and weathering in particular governs the relative amounts of cations and silica as well as the pH of waters across Southland. It is also important in terms of the organic content of geologic materials as this has important consequences for the redox status of the saturated and unsaturated zone which plays a crucial role in the concentration of nitrates (i.e. influence denitrification potential). Finally, it also governs the hydrology in terms of whether there is significant bypass flow through macropores in the soil zone and the relative rate of groundwater movement (B. Hughes, Wilson, Rissmann, & Rodney, 2016).

It has been found that soil zone water interactions appear to be the primary source of Ca and alkalinity across Southland with no significant differences observed between soil water and under-saturated (in terms of Ca minerals) oxidised ground and surface waters. The significance of this is that it appears that water rock interaction do not contribute significantly to the Ca or alkalinity of surface waters in Southland (Rissmann et al., 2016d). Calcium accumulates in the soil zone over the summer months due to minimal flushing events and evaporation. This Ca is not nearly as strongly bound as that within rock and can thus be readily flushed from the soil zone during high rainfall events. Calcium sourced from water-rock interactions within the saturated zone is a much slower process and hence is a much more gradual source of calcium. A number of other factors also influence hydrochemistry including local topography, clay formation and exchangeable bases.

Taken all together regional differences in these factors largely determine local hydrochemistry. The Waimea catchment itself consists of four principal physiographic units, bedrock/hill country, gleyed, oxidising and old Mataura (B. Hughes et al., 2016). The result of this is that trends and differences in these four key drivers have been shown to be useful indicators of local water chemistry in any given area across Southland.

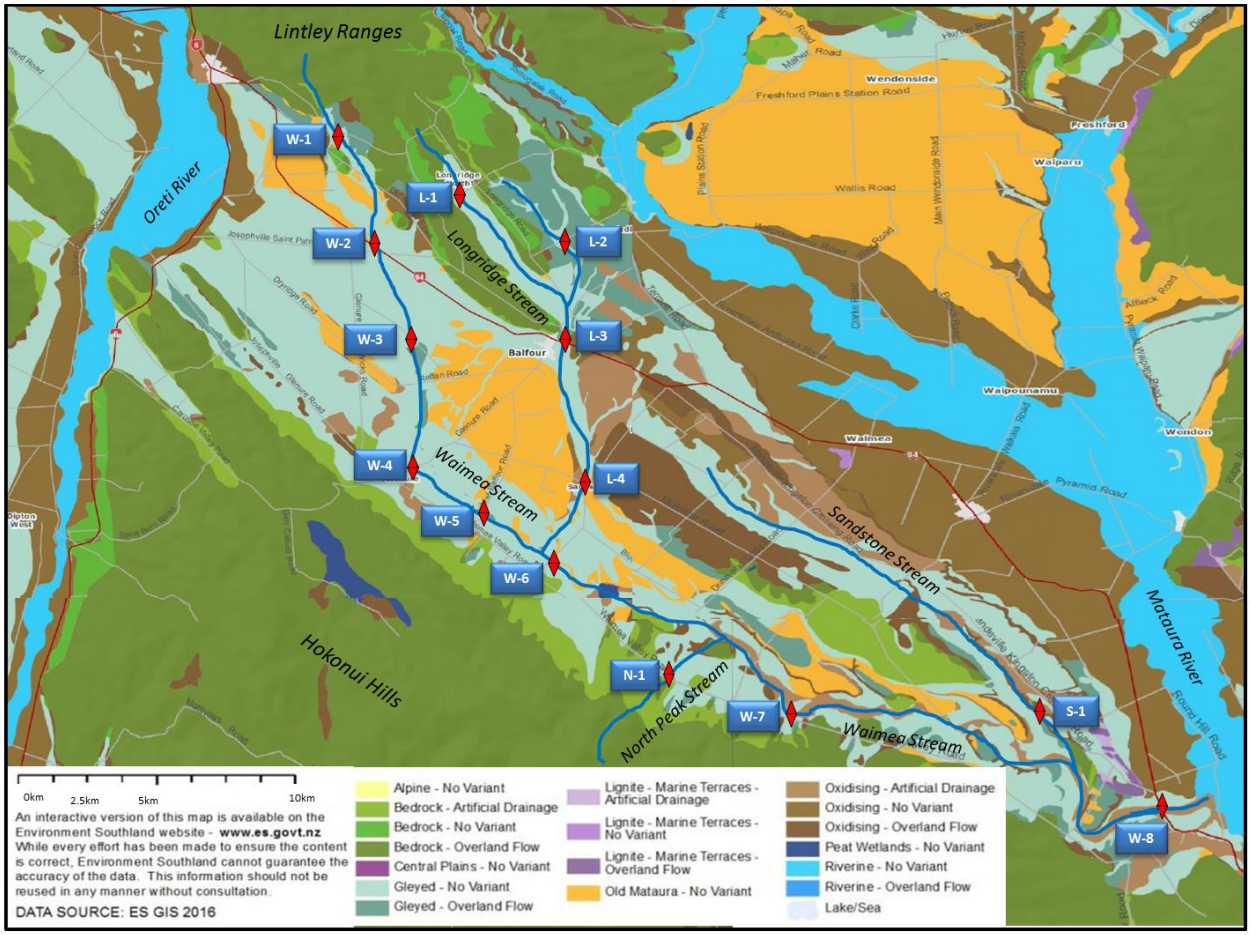

Figure 1-15 Pysiographic map of the Waimea catchment (see key on map for the unit types). Surface water monitoring sites on the Waimea Stream (W-1 to W-8), Longridge Stream (L-1 to L-4), North Peak Stream (N-1), and Sandstone Stream (S-1) are displayed. This map has been adapted from a map produced by Environment Southland (Rissmann et al., 2016a).

Bedrock/Hill country

This physiographic unit is characterised as areas receiving coastal or inland precipitation that then travels through highly weathered soils on rolling to steep terrain. Flow is principally derived from overland flow with periodic high flows driven by significant rainfall events. Waters tend to have low electrical conductivity which reflects the water source of dilute source water and overland alpine flow. Higher electrical conductivities during low flow has been interpreted as the result of a greater influence of groundwater on flow. Water facies are mainly sodium dominated (Na-HCO_3 and Na-Cl) waters.

This unit makes up the head waters of the Waimea stream which originates within the Lintley range to the north of the Waimea plains. The hilly country around the upper reaches of Longridge Stream along with the Hokonui Hills that lie along the Southern edge of the Waimea Plains also consist of the bedrock/hill country physiographic unit (Figure 1-15).

Gleyed

These are areas where there is some potential for denitrification to occur within the soil profile, mostly as a result of poor subsurface drainage. Solute loads range from high in coastal areas to low in inland areas. The level of total dissolved solids in precipitations plays an important role in the

chemical facies of surface water. Precipitation that is high in solutes will produce Na-Cl-HCO_3 type waters whereas precipitation low in solutes will produce Ca-Na-HCO_3-Cl Waters.

This unit has high denitrification potential which is a reflection of the poorly drained soils with high organic carbon content. As a result groundwater below this unit tends to have low nitrate concentrations. The amount of denitrification that occurs is largely dependent on resident time within the soil with longer resident times allowing for greater denitrification to occur. Surface waters tend to show elevated iron and manganese levels as a result of a reducing soil zone as well as slightly enriched ^{13}C-DIC composition resulting from DIC within a reducing environment.

The relative proportion of water that goes into deep drainage through to groundwater is relatively low. Rather, a greater proportion tends to exit the soil zone as overland flow. This results in solutes exiting the soil zone system during high rainfall events as poorly bound solutes that have accumulated within the soil zone (top 60 cm) are flushed into streams and river. Artificial drainage such as mole tile drainage system can enhance this effect of episodic solute discharges. During such events solute levels can show order of magnitude increases during high rainfall, high lateral flow events (B. Hughes et al., 2016).

The gleyed physiographic unit makes up a large proportion of the Waimes Plains, especially in the upper north-western area (Figure 1-15)

Old Mataura

This unit comprises areas that consist of highly weathered, older terraces that contain oxic waters that are not connected to main stem rivers. This area consists of flat well drained soils. Waters from this unit reflect land surface recharge resulting from spill over from Southland's northern ranges that go on to interact with highly weathered soils. Due to its inland location marine aerosols (Na-Cl) are relatively low. Water facies in this area are Na-Cl, Ca-HCO_3 and Ca-Cl type waters which is a reflection of land surface recharge into highly weathered soils and an unsaturated zone with low base saturation (low in Ca, Mg, K, Na).

Oxic waters along with the low carbon contact of the soil zone means that these areas have a low potential for denitrification to occur. Consequently, groundwater nitrate concentrations are very high. The 'Balfour nitrate hotspot' is an example of this, with nitrate (NO_3-N) levels between approximately 10-20 mg/L. Isotopic compositions of δ^{18}O-H_2O in groundwater tend to be depleted which indicates a significant proportion of recharge occurs as spill over from ranges to the north such as the Garvie Mountains (B. Hughes et al., 2016).

This physiographic unit is centred around Balfour on the Waimea Plains and largely coincides with the 'Balfour nitrate hotspot'. There are also areas of it to the north-west and south-west of Balfour, as well as a significant section at the northern extremity of the Waimea Plains (Figure 1-15).

Oxidising

This area is characterised by an oxic soil zone and groundwater that has limited hydrological connectivity to main stem rivers. It is characterised by undulating topology with fine textured soils which can have varying degrees of sub soil permeability. Soils in this area show little denitrification potential, which coupled with low levels of main stem flushing lead to highly elevated groundwater nitrate concentrations. Water facies in the unit reflect local land-surface recharge reacting with soils with a high base saturation leading to Na-Cl, Na-HCO_3 and Ca-Cl type waters.

The unit has elevated potassium, sulphate and nitrate concentrations which is a reflection of the dominance of soil surface recharge and the relatively young age of the geomorphic surfaces. Lower organic carbon in the soil zone results in lower respiration and CO_2 levels which means the soil has limited alkalinity (B. Hughes et al., 2016)

The majority of this physiographic unit on the Waimea Plains lies to the east of Longridge Stream (Figure 1-15).

Chapter 2 Methods

This investigation consisted of two parts. The first part involves the analysis of data previously collected by Environment Southland on the Waimea Catchment over the period from 2000 to 2013. The second section consists of additional data collected on the Waimea Catchment during the first half of 2016 from February through to July. Data collection undertaken in 2016 was done in order to further investigate the findings drawn from the Environment Southland data analysis. In this chapter the methods employed in the analysis of the data collected by Environment Southland are described, along with a description of the sampling and data analysis methods used during the 2016 monitoring programme.

Environment Southland has collected data from five sites along the Waimea Stream (W-1,3,5,7,8), along with data for Longridge Stream (L-4), Sandstone Stream (S-1) and North Peak Stream (N-1). For the second part of this investigation, data was collected for eight sites along the Waimea Stream (W-1,2,3,4,5,6,7,8) along with four sites along Longridge Stream (L-1,2,3,4). Data has also been collected from a number of bores across the Waimea Plains by Environment Southland. During 2016, a groundwater sample was taken from bore E44/0036 (for map Figure 2-1).

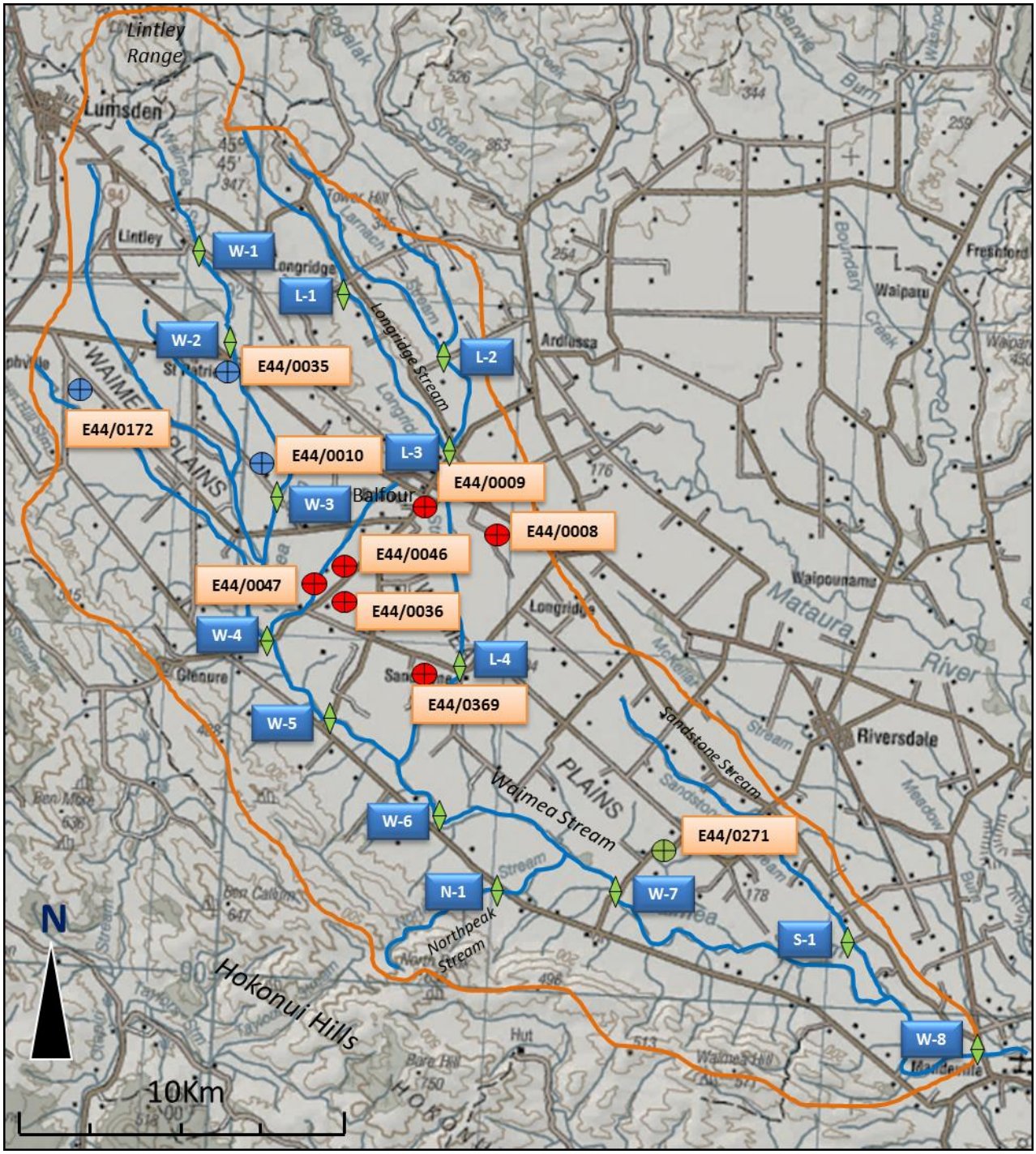

Figure 2-1 Surface water and groundwater monitoring sites. Surface water monitoring sites on the Waimea Stream (W-1,,2,3,4,5,6,7,8), Longridge Stream (L-1,2,3,4), North Peak Stream (N-1) and Sandstones Stream (S-1) are displayed (green diamonds). Yellow crosshairs represent groundwater bores and are in three groups (blue= upper Waimea, red= Balfour nitrate hotspot, Green= lower Waimea). The orange line is the approximate catchment of the Waimea Stream.

2.1. Environment Southland data analysis

Environment Southland has been collecting hydrochemical data on the Waimea catchment for groundwater since 2000, and for surface water since 2005. For this study Environment Southland kindly allowed access to this data set. For surface water basic water quality data was collected monthly between 2005 and 2014 including data on nutrient concentrations. Over the period from

September 2012 to June 2014 a full suite of hydrochemical data (including major ion and some trace elements) was collected monthly at each site.

Analysis of this data involved four parts:

1. Characterisation of spatial and seasonal variation in surface water chemistry.
2. Characterisation of groundwater chemistry.
3. Characterisation of groundwater and surface water nutrients.
4. Relate in-stream chemistry to in-stream nitrate concentrations.

Surface water chemistry was analysed for both spatial variation (i.e. between each site), and for seasonal variation, in particular, between summer and winter. This was done in order to establish the chemical characteristics of summer low flows and winter high flows. Groundwater was then analysed in order to establish its chemical character and identify any possible chemical signatures that may be used to identify significant inputs to surface waters. From this the chemical characteristics of the low groundwater dominated flow and the high overland dominated flow end-members were identified. Nutrient concentrations for surface water were analysed for both spatial and seasonal variation. Groundwater nitrate concentrations were also analysed to reaffirm where groundwater nitrate is elevated. Nutrient concentrations were then integrated with the end-members identified in the first two parts in order to establish which end-members are contributing nitrates to the Waimea Stream, when and where.

2.2. 2016 monitoring programme

There were three principal components to this monitoring programme:

Basic water quality:

- Basic water quality – pH, conductivity, temperature, dissolved oxygen, flow and basic observation of periphyton and macrophyte cover.
- Nutrients – nitrate and dissolved reactive phosphorus (DRP).
- Water chemistry, including major ions and trace metals.

Stable Isotopes:

- Stable hydrogen and oxygen isotopic composition.
- Stable carbon isotopic composition.

Sediment analysis

- Analysis of chemistry of the sediment at each site via a grab sample collected in February.

The months of February to July were monitored in order to get coverage of the shift between dry low flow summer conditions prevalent in late summer, to wet high flow condition prevalent over the winter months.

2.2.1. Sampling sites

To get full coverage of the Waimea catchment twelve sampling sites were chosen. Half of these sites were the same as those used by the Environment Southland Waimea Stream monitoring programme in order to provide for continuity of, and comparability with, Environment Southland data. In addition to these six sites another six sites were chosen to try and gain a fuller understanding of

where nutrient and contaminant inputs may be occurring, as well as the dynamics of surface water-ground water interactions. Eight of the sites are on the Waimea Stream itself, while the remaining four are distributed along Longridge Stream, including one on a major tributary of Longridge Stream, Larnach stream (Figure 2-1). Two sites within the Waimea catchment monitored by Environment Southland were not monitored in this programme as they were less relevant to this study; two tributaries of the Waimea Stream, North Peak Stream and Sandstone Stream (Table 2-1).

Table 2-1 Details of surface water and groundwater monitoring sites on the Waimea Stream (W-1 to W-8), Longridge Stream (L-1 to L-4), Sandstone Stream (S-1), and North Peak Stream (N-1), along with bore E44/0036.

Site Number	Site Name	Coordinates: Latitude, Longitude	Distance from Waimea/Mataura Confluence (Km)	Previous Data
Waimea Stream				
W-1	Old Balfour Rd	-45.767164, 168.491821	35.86	Water quality
W-2	Saint Patricks	-45.804153, 168.516197	31.59	
W-3	Murphy Rd	-45.839803, 168.533192	28.21	Water quality
W-4	Glenure Rd	-45.876624, 168.528900	26.23	
W-5	Pahiwi-Balfour Rd	-45.898252, 168.549500	23.76	Water quality
W-6	Waimea Valley Road	-45.925483, 168.592243	19.46	
W-7	Nine Mile Rd	-45.944943, 168.660393	13.79	Water quality
W-8	Mandeville	-45.987301, 168.80064	1.94	Water quality & Flow.
Longridge Stream				
L-1	Longridge School	-45.783686, 168.557053	31.10	
L-2	Wilson Rd	-45.803555, 168.595161	27.46	
L-3	Lumsden/Riversdale	-45.838009, 168.596191	24.57	
L-4	Sandstone	-45.886304, 168.601856	20.93	Water Quality
Sandstone Stream				
S-1	Kingston Crossing	-45.950434, 168.745708	8.12	Water Quality
North Peak Stream				
N-1	Waimea Valley Road	-45.943272, 168.617477	16.60	Water Quality
Groundwater				
E44/0036	Steven's Bore	-45.867797, 168.550647	25.47	Water Quality

2.2.2. Sampling method

Water samples were collected from surface water at each site on a monthly basis from February 2016 through to July 2016 in order to capture shifts that may occur in the Waimea stream hydrology and chemistry from base flow conditions over late summer through to peak winter flows.

Surface water

An HQ40d portable probe was used to record water pH, conductivity, dissolved oxygen, and temperature at each site. The probe was tested prior to use against standards for pH, conductivity and dissolved oxygen and was calibrated when necessary. A DR 900 Multiparameter Handheld Colorimeter was used to get preliminary data for nitrate and phosphate concentration to which lab data could be compared, and to get a measurement of turbidity.

Water sampling was carried out by collecting grab samples that were upstream of the bridges at each site to avoid samples contaminated with any potential localised contaminants from the road. Samples were collected at the same site where flow gauging was carried out at a roughly one monthly interval. Samples were collected either in a single day or over two consecutive days on each sampling run.

Water samples were collected into six different bottles at each site for the different types of lab analysis to be undertaken. All samples were kept as cool as practical and out of direct sunlight, with the nutrient samples being stored in a chilli bin with ice. Once back in Christchurch, the samples were stored in a fridge at Lincoln University with the nutrient samples being kept in a freezer. Unfiltered samples were collected in to two 50ml PET centrifuge tubes for unfiltered trace metal analysis and nutrient analysis. Samples were filtered through 0.45 µm filters for dissolved trace metals, major ions and oxygen and hydrogen samples. As little headspace was left as practical so as prevent atmospheric exchange with the sample. For carbon isotope samples, samples were first filtered through a 0.45 µm filter, before 2ml was drawn up into a syringe and injected into airtight helium flushed vial.

Flow gauging

Flow gauging was carried out at each site with a global water flow probe. Gauging could not be carried out when either the stream was too small, or stagnant to be measured, or indeed too large to be safe to cross on foot. Flow data for the site at Mandeville was obtained from Environment Southland's flow gauge. Gauging cross sections were chosen at each site perpendicular to flow and divided into sections of roughly uniform depth and flow, based on observations of the stream topography and preliminary flow readings across the stream's reach. Each of these sections was then measured in width, depth and flow velocity. The flow in volume per second was calculated from each section and then summed to give an overall flow. Flow readings were gathered over a 30 second period for each section.

Groundwater

Sampling of groundwater from bores was limited as these mostly lie on private land and require special pumping equipment to draw up the water. However, a groundwater sample was taken from bore E44/0036 during the February sampling run. The sample was taken and subsequently treated the same as surface water samples above.

Sediment

A sediment sample was collected at each site into a 250 ml PET pottle. Sediment was collected as near as practical to the stream thalweg so as to avoid any particularly local sediment input, such as a nearby eroding bank, and to maximise the representativeness of the sample for the general area. Samples were of the top 5-10cm of sediment on the stream's bed.

2.2.3. Analytical methods

Nutrients

Dissolved reactive phosphorous, total nitrate/nitrate and DIC were analysed at the Waterways Centre laboratory at Lincoln University. Nitrate-Nitrite nitrogen (NO_3 + NO_2) was determined using a colometric method whereby nitrate is reduced almost quantitatively to nitrite in the presence of cadmium. The nitrite that is produced is then diazotized with sulphaniamine and is then coupled with N-(1-Naphthy1)-Ethylenediamine didrochloride which forms a highly coloured dye that is measured calometrically to determine the total nitrate-nitrite concentration of the sample which is calculated with reference to a standard curve produced from known nitrate concentrations (Eaton, Clesceri, Greenberg, & Franson, 1995)

Dissolved reactive phosphorus (DRP) was determined using a colometric method. Ammonium molybdate plus antimony potassium tartrate reacts with orthophosphate in an acidic medium to form phosphomolybdic acid. Phosphomolybdic acid is then reduced to molybdenum blue by ascorbic acid. The resulting colour is then measured colometrically and the concentration of total reactive phosphorus are calculated against a standard curve produced from known phosphorus concentrations (Caspers, Mackereth, Heron, & Talling, 1979).

Dissolved inorganic carbon

DIC was determined using an infrared gas analyser (IRGA). The water sample is acidified with phosphoric acid under a nitrogen head space. The acidification converts all DIC to carbon dioxide which then equilibrates with the nitrogen headspace. The carbon dioxide is then injected into the IRGA and DIC values are determined with reference to standard bicarbonate solutions (Hawes, Safi, Webster-Brown, Sorrell, & Arscott, 2011).

Anions: Ion exchange chromatography

Chloride, sulphate and bromide were analysed by the Department of Soil and Physical Sciences department at Lincoln University using ion exchange chromatography.

Major ions and trace metals: ICP Mass spectrometry

Major cations, metals and trace metal were determined by the Chemistry Department at the University of Canterbury using ICP mass spectrometry.

Stable Isotopes: ICP mass spectrometry

Isotope fractions were determined by the Geology Department at the University of Canterbury using ICP mass spectrometry.

Sediment digest

Sediment samples were initially sieved through a 63 µm mesh and the fines were collected into 15 ml PET tubes. Approximately 0.1g of 63 µm sediment was then weighed accurately into Teflon beakers to which concentrated HNO_3 acid was added. The beakers were then heated on a hot plate with a lid on until the samples were almost dry. The lid sits loosely on the top of the beaker, allowing moisture and pressure to escape. The beakers were then filled with 45 mL of 0.1 *N* HNO_3 and heated with the lid on for a further hour. The 0.1 *N* HNO_3 solution was made by diluting concentrated HNO_3 with deionised water. The lids were then taken off and the sample was heated until the solution volumes were reduced to less than 10 mL. The samples were then transferred to a 15 mL PET tube

which was then made up to a known weight of approximately 10g with 0.1 *N* HNO_3. Major cations, metals and trace metals were determined using ICP mass spectrometry as described above.

2.3. Data Analysis

The focus of data analysis involved investigating correlations, patterns and associations between different pairs of parameters, for example, between in-stream flow and nitrate concentrations. As a basic measure of the strength of correlations, linear correlation coefficients have been used where appropriate. Graphpad Prism, version 7, was used for statistical analysis.

2.3.1. Spearman's rank correlation coefficient

Correlations were also investigated using Spearman's rank correlation coefficient. This is a measure of correlation that is used for data sets that are not normally distributed, have a large amount of 'noise' and are potentially exhibiting a non-linear relationship. It is also useful for data sets that may contain outliers. The correlation coefficient is determined by replacing the values of *x* and *y* with their ranks, such that the smallest *x* is assigned a 1, the smallest *y* a 1, the next largest a 2 until all values have a rank. This is then converted in a Spearman rank correlation coefficient which gives a score relating how well the two sets of ranking match up. A value of 0 would indicate no correlation, either positive or negative between the two variables, +1 indicates a perfect positive correlation, meaning every ranking of *x* and *y* match. A value of -1 indicates a perfect negative correlation between *x* and *y (Borradaile, 2003).*

$$R_S = 1 - \frac{6\sum_{i=1}^{n} d_i^2}{n(n^2-1)}$$

di=r(xi)-r(yi) (the difference in ranks between the two variables for each sample)
n=number of samples
R_s=spearman rank correlation coefficient

2.3.2. Other statistical methods

Elements of this study also involved the interpretation of data which does not include any formal statistics. This could be for example the grouping of data between summer and winter and assessing whether this grouping corresponds to shifts in particular variables, such as nitrate concentration, ion ratios, or stable isotope compositions. Such groupings were then assessed using t-tests and analysis of variance (ANOVA) where appropriate to establish whether groupings formed thusly were significantly different.

2.4. Quality control and study error estimation

2.4.1. Sampling

Sampling in this study was generally carried out near bridges. Road run off from cars debris and fuels is a possible point source of contamination which could skew the data collected on for example trace metal content. To ameliorate this, sampling was carried out upstream of bridges (> 5m). One site (W-6) was not in the proximity of a bridge and thus acted as a control site.

Samples were collected and analysed as soon as was practicable. In order to ensure samples were stable they were kept as cool as possible and put in a fridge as soon as possible. Water samples for nutrient analysis were kept on ice and in the dark at the sampling site for transport back to the laboratory.

2.4.2. Lab analyses

Nutrients

Total nitrate+nitrite along with DRP were analysed with reference to a standard curve produced from a stock solution of a known concentration. The linear regression for standard curves used had an r^2>0.99. The detection limit for the DRP method used is 10 µg/L (Caspers et al., 1979). The nitrate method had a detection limit of 0.06 mg/L, which was calculated using the following formula:

LOD=(a/b)X3.3

Where:

LOD= limit of detection
a= standard error of standard curve linear regression
b= slope of the standard curve linear regression

Major ions

DIC (DIC) was determined with reference to a standard curve with a linear regression with an r^2>0.99. The detection limit for DIC has been calculated as three times the standard deviation of six blank samples that were analysed. The detection limit calculated is 2.4 mg/L.

In order to determine the error of the analysis of major ions (Ca,K,Mg,Na,SO_4,Cl,HCO_3) an ion balance was undertaken (see appendix A). Major ions make up most of the dissolved charged species in freshwater, thus the total charge of the major anions should equal the charge of the major cations. As a percentage difference in charge between total anions and total cations, 99.2% of samples had <10% difference, while 0.8% had <15% difference.

Trace metals

The certified reference material NIST CRM 1643 was used by the Geology Department, when carrying out inductively coupled mass spectrometry. Detection limits have been determined as three times the standard deviation of the concentration of elements in the blank samples that were analysed (Table 2-3).

Sediment digestion

A certified reference material (CRM) (PACS-2, National Research Council, Canada) was digested and analysed in order to determine the percentage recovery of the method used. The percentage recovery is the amount of an element detected in the CRM relative to the amount that is actually in the CRM as specified by the supplier. Not all of the elements analysed for were present in the CRM.

Fe was found to be over range for the analysis used. Hence in the reported data Fe is missing.

Recovery rates of the CRM are displayed.

Table 2-2 Sediment digest CRM recovery rates

Element	Recovery rate%	Element	Recovery rate%
Na	75.1	Co	83.4
Ca	55.0	Cr	32.0
Mg	75.0	Ni	90.3
K	31.8	Cu	94.0
Al	30.3	As	85.8
Mn	64.4	Mo	79.5
Ti	31.1	Cd	91.1
Zn	84.3	Sb	0.12
V	67.9	Pb	73.0

Detection limits

The analyte, method used, and detection limits for water samples (Table 2-3).

Table 2-3 Detection limits of water analyses.

Analyte	Method used	Detection limit
Nitrate	Colorimetry	0.06 mg/L
Dissolved reactive phosphorus	Colorimetry	10 µg/L
HCO_3	Infrared gas analyser	2.4 mg/L
Cl	Anion chromatography	0.005 mg/L
Br	Anion chromatography	0.02 mg/L
SO_4	Anion chromatography	0.05 mg/L
Na	ICP mass spectrometry	6.1 µg/L
Mg	ICP mass spectrometry	4.7 µg/L
K	ICP mass spectrometry	2.3 µg/L
Ca	ICP mass spectrometry	8.1 µg/L
Al	ICP mass spectrometry	0.8 µg/L
B	ICP mass spectrometry	0.3 µg/L
Fe	ICP mass spectrometry	0.008 µg/L
Mn	ICP mass spectrometry	1.7 µg/L

Chapter 3 Results: Analysis of Existing Environment Southland Data

Environment Southland monitoring data has been collected for surface water over a period from 2004 to 2015, and for groundwater over the period from 2000 to 2015. Surface water quality has been collected on a monthly basis at eight sites within the Waimea catchment (for map see Figure 3-1). Five of the sampling sites are on the Waimea Stream itself (W-1, W-3, W-5, W-7 and W-8) and are spread along its length, from where it exits the Lintley Range at its headwaters, to near its confluence with the Mataura at Mandeville. Data has also been collected for three tributaries of the Waimea Stream; Longridge Stream (L-4), Sandstone Stream (S-1) and North Peak Stream (N-1). Over this period monthly data was collected on nutrient levels, as well as a raft of basic water quality parameters. An in depth monthly monitoring programme was carried out over the period from September 2012 to June 2014, which produced a full suite of hydrochemical data for the eight sites.

This chapter involves the analysis of data collected by Environment Southland. Firstly, the climatic conditions and flow of the Waimea Stream, for the period in which the comprehensive suite of hydrochemistry data was collected (September 2012 to June 2014), is displayed. This was done in order to be able to relate in-stream chemistry to hydrological conditions within the Waimea catchment.

Secondly, an overview of both surface and groundwater hydrochemistry was produced. The aim of this was to establish the hydrochemical character of different end-member inputs to in-stream flow, particularly the groundwater end-member vs overland flow end-member. This was achieved by examining differences in in-stream chemistry between low base-flow conditions and high flood flow conditions. Hydrochemical data of groundwater across the Waimea Plains was used to directly characterise the chemical characters of the groundwater end-member. The aim of this was to establish tracer or chemical signatures of different end-members within the Waimea catchment.

Thirdly, nutrient concentrations in both surface and groundwater were analysed. Surface water was analysed for both spatial and seasonal variation, while groundwater was analysed for spatial variation and for any long term trends in water quality and chemistry.

Fourthly, the end-member signatures identified were integrated with the nitrate dynamics in order to establish the pathways (hydrological end-members) or sources of nitrate entering the Waimea Stream. This involved correlating in-stream end-member chemical tracers identified with in-stream nitrate. This was done in order to establish a link between a particular end-member and elevated in-stream nitrate.

Finally, hypotheses regarding the hydrochemical signature of groundwater and overland flow end-members entering the Waimea Stream are presented, along with identified flow paths by which nutrients enter the Waimea Stream. These hypotheses will then be tested in chapter four.

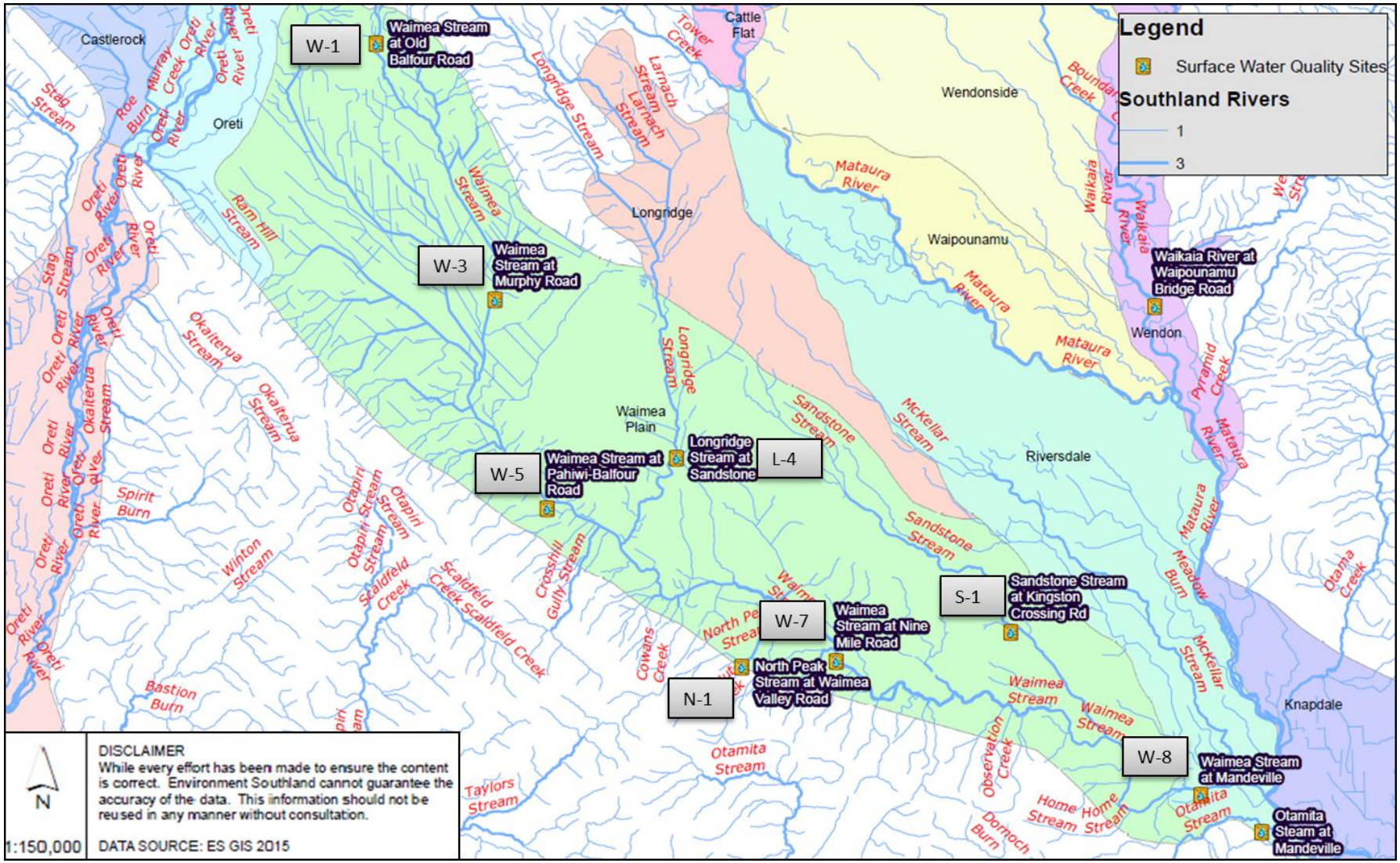

Figure 3-1 Environment Southland surface water monitoring sites on the Waimea Stream (W-1, W-3, w-5, W-7 & W-8), Longridge Stream (L-4), North Peak Stream (N-1) and Sandstones Stream (S-1). The different coloured shadings relate to different groundwater zones (zones named in black text). The map has been adapted from a map of surface water monitoring sites produced by Environment Southland (D. May, personal communication, December 15 2015).

3.1. Climatic conditions during monitoring period

In this section the rainfall, potential evapotranspiration and in-stream flow during the monitoring period from September 2012 to June 2014 is presented. Rainfall and Penman potential evapotranspiration data was obtained from NIWA, from a monitoring station at Riverdale, York Road (station number: 38645. Latitude: -45.904, longitude: 168.739) (NIWA, 2016), while average monthly rainfall for the Waimea Plains, along with the flow of the Waimea Stream at Mandeville (W-8), has been obtained from Environment Southland (Environment Southland, 2016).

The long term average monthly rainfall does not fluctuate greatly between summer and winter, with the lowest average rainfall occurring during July with 53mm, which compares to 85mm during November. There was a clear seasonal difference in the levels of evapotranspiration occurring, where during summer it exceeds the average monthly rainfall, while during winter, the level of evapotranspiration occurring approaches 0 mm. Accumulated monthly rainfall during the study periods ranged from <20mm, to in excess of 160 mm. There was no clear difference between summer rainfall levels and winter (Figure 3-2). An excess of rain in relation to evapotranspiration appears to be the key driver of soil moisture levels and hence whether there is likely to be significant levels of overland flow.

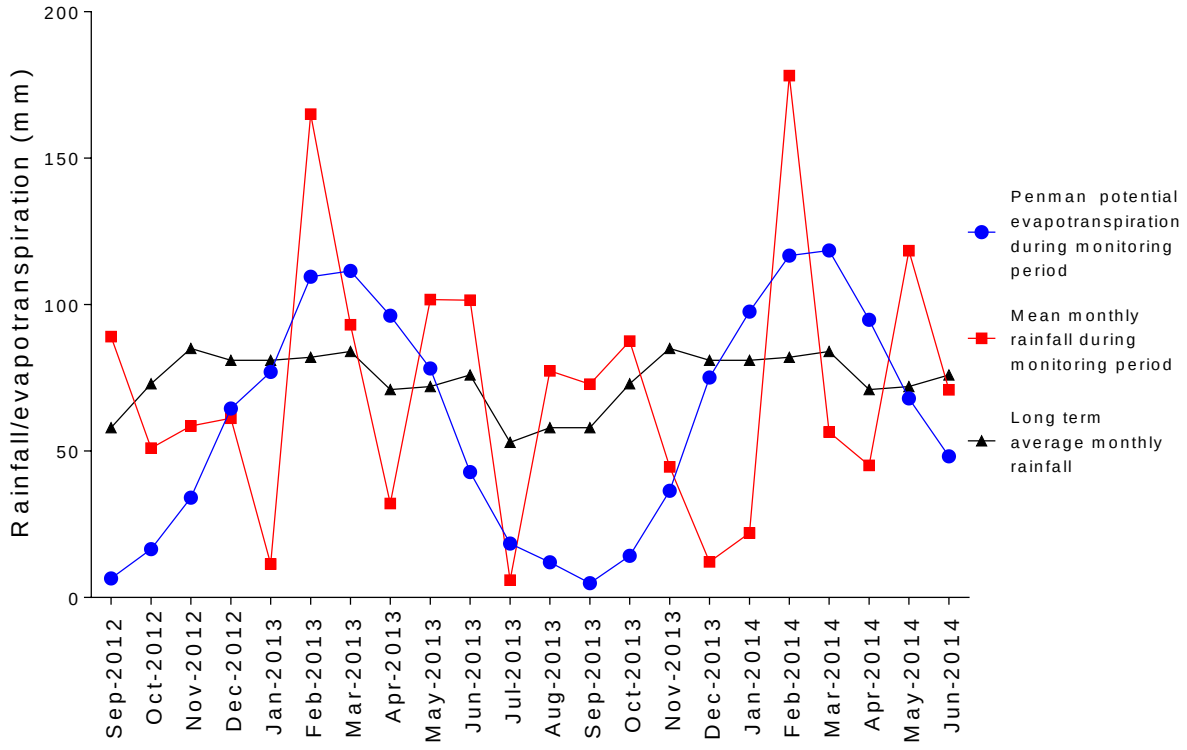

Figure 3-2 Monthly accumulated rainfall and Penman potential evapotranspiration of the Waimea catchment for the study period September 2012 to June 2014, along with the long term average monthly accumulated rainfall. Monthly accumulated rainfall and Penman evapotranspiration data for the study period has been obtained from NIWA (NIWA, 2016), while long term average monthly rainfall has been obtained from Environment Southland (Environment Southland, 2016).

Flow levels in the Waimea Stream during the study period on the day of sampling ranged from less than 0.5 m^3/sec to approximately 7.9 m^3/sec. Flow levels were consistently below 1.0 m^3/sec during February, March and April during both 2013 and 2014, while during July flow levels were as high at 7.9 m^3/sec. Flow on the day of sampling appears to fit closely with flow conditions on the prior seven days before monitoring was carried out (Figure 3-3).

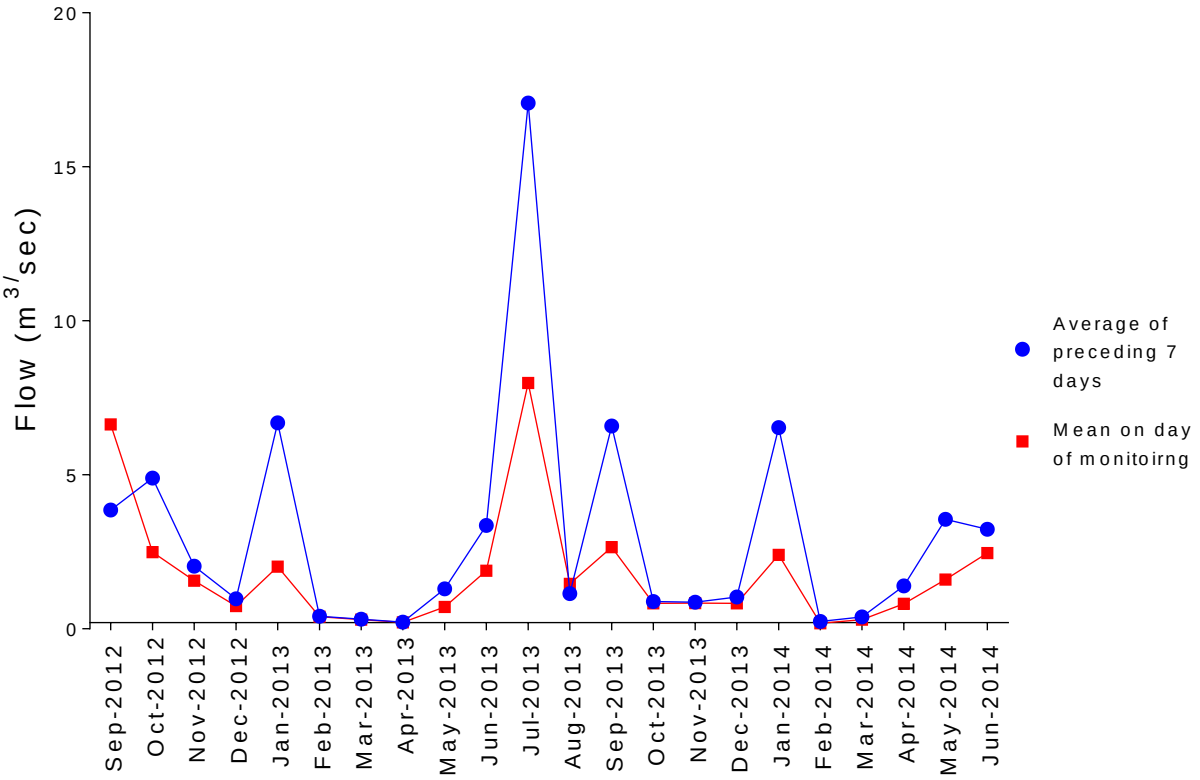

Figure 3-3 Waimea Stream flow at Mandeville on the day of monitoring along with the mean flow of the preceding week to monitoring over the period September 2012 to June 2014. Flow data for the Waimea Stream at Mandeville has been obtained from Environment Southland (Environment Southland, 2016).

3.2. Surface water chemistry

In this section, water quality and hydrochemistry was characterised over the period September 2012 to June 2014. Firstly, spatial differences in hydrochemistry and water quality were examined across the Waimea and tributary sites. Secondly, temporal variation in in-stream chemistry was analysed. Major ion ratios are investigated along with any significant differences in major ion proportions between summer and winter. Temporal dynamics of month to month hydrochemistry is then analysed for significant difference between the summer and winter months.

3.2.1. Basic water quality

For the Waimea Stream and tributaries, the pH remained approximately between 7 and 8. There was no statistically significant difference in pH between the two sites in the upper catchment, at W-1 and W-3, nor between the three sites in the lower half of the catchment (p-value > 0.05). There was however a significant increase in pH between W-3 and W-5 (p-value < 0.05), where the median value increases from 7.5 to 7.7. All sites of the Waimea Catchment had median dissolved oxygen levels that exceeded 100%. The temperature at all sites had a wide range with values ranging between approximately 4° C and 17° C, with no significant differences between sites apart from between L-4 and W-1, which recorded median temperatures of 12.25 °C and 9.7 °C respectively (p-value < 0.05) (Figure 3-4).

Conductivity increased significantly between W-1, W-3 and W-5 (p-value < 0.05) (Figure 3-4). Median conductivity at W-1 was 92 µs/cm, at W-3, 155.5 µs/cm, and at W-5, 210 µs/cm. Median conductivity then dropped significant between W-5 and W-7, to approximately 192 µs/cm, at the two lower sites on the Waimea Stream (W-7,8) (p-value < 0.05). The conductivity of N-1, a hill-fed stream, was significantly lower than that of

the two lowland tributaries of the Waimea Stream, Longridge and Sandstone Streams (L-4, S-1) (p-value < 0.05) (Figure 3-4).

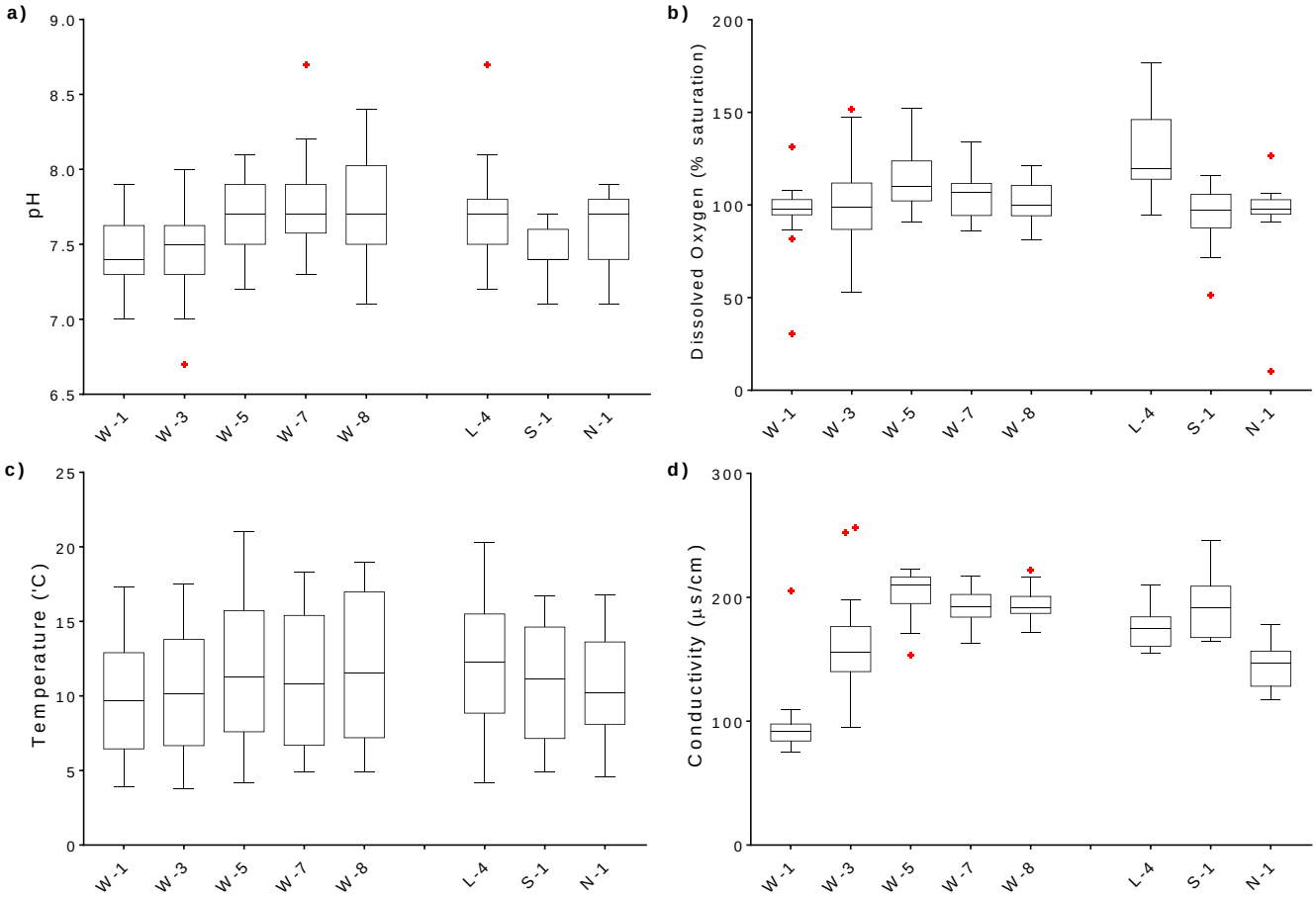

Figure 3-4 Basic water quality of the Waimea catchment. Water quality was monitored by Environment Southland for 22 months from September 2012 to June 2014 at different sites along the Waimea Stream (W-1,3,5,7,8), Longridge Stream (L-4), North Peak Stream (N-1) and Sandstone Stream (S-1) (for locations see Figure 3-1) and the a) pH, b) dissolved oxygen as percentage saturation, c) temperature and d) conductivity were determined monthly. Tukey plots with the median and interquartile range from 22 measurements are displayed. The whiskers represent 1.5 X interquartile range. Outliers are marked by red crosses.

3.2.2. Spatial variation in surface water chemistry

Major ions

The trend in a number of major ions reflected the observed increase in conductivity on the Waimea Stream between W-1 and W-5. Concentrations of HCO_3, Cl, Ca, Na, Mg, and Si all increased by two to four-fold between W-1 and W-5, with W-3 having intermediate concentrations between the two sites (p-value < 0.05). SO_4 and K concentrations approximately doubled between W-1 and W-3 (p-value < 0.05), with levels remaining thereafter relatively steady through to W-8. There was a significant upward spike in Si concentrations at W-5, from a median of approximately 11.5 mg/L at W-1 and W-3, to approximately 15.5 mg/L at W-5 (p-value 0.05). Si concentrations then significantly dropped to approximately 11.5 mg/L at W-8 (p-value < 0.05). Mg was also significantly higher at W-5 compared to other sites on the Waimea Stream, with a median of 7.9 mg/L, compared to 4.5 mg/L at W-3, and approximately 6.4 mg/L at W-7 and W-8 (p-value < 0.05).

North Peak Stream (N-1) had slightly, yet significantly, elevated Cl and Na concentrations compared to W-1, the other predominantly hill-fed site (p-value < 0.05). SO_4 and K concentrations for N-1 were relatively low and were similar to W-1, with a median SO_4 concentration of 5.85 mg/L. In contrast to W-1 however, median Ca concentrations were approximately double that of W-1 (p-value < 0.05). Longridge (L-4) and Sandstone (S-

1) stream had similar SO_4, Na, and K concentrations to the lower sites on the Waimea Stream. Sandstone Stream had significantly higher Si concentrations than any other site monitored within the Waimea catchment, with a median Si concentration of 22.55 mg/L (p-value < 0.05) (Figure 3-5).

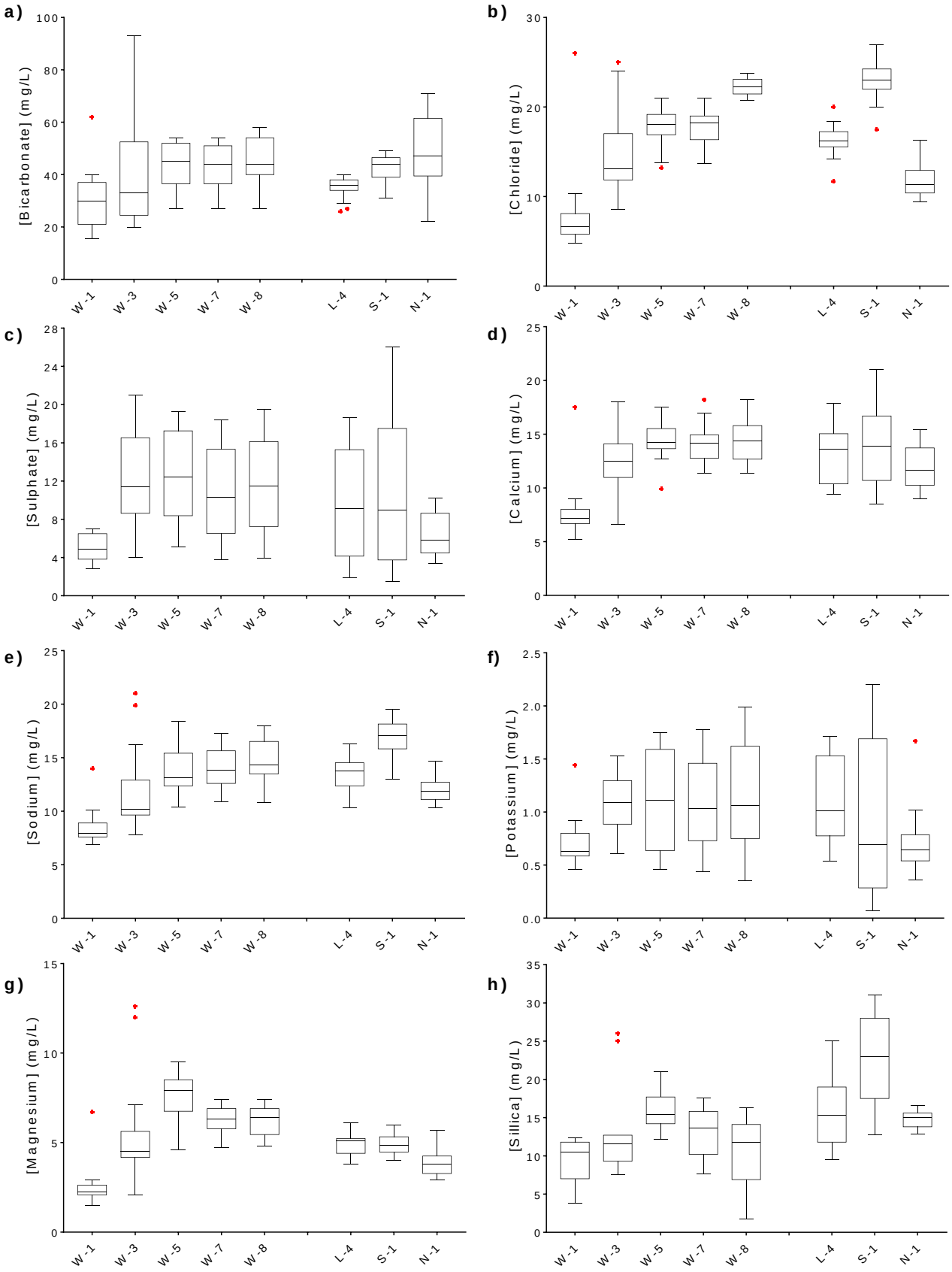

Figure 3-5 Major ion chemistry of the Waimea catchment. Water chemistry was monitored by Environment Southland for 22 months from September 2012 to June 2014 at different sites along the Waimea Stream (W-1,3,5,7,8), Longridge Stream (L-4), North Peak Stream (N-1) and Sandstone Stream (S-1) (for locations see Figure 3-1) and the dissolved concentration of a) bicarbonate, b) chloride, c) sulphate d) calcium, e) sodium, f) potassium, g) magnesium, and h) silica were determined monthly. Tukey plots with the median and interquartile range from 22 measurements are displayed. The whiskers represent 1.5 X interquartile range. Outliers are marked by red crosses.

Trace metals

Environment Southland collected data on two trace metals, dissolved Fe and Mn. These dissolved trace metal concentrations did not appear to show the same pattern as the bulk of major ions in terms of increasing steadily between W-1 and W-5 on the Waimea Stream. Manganese concentrations were significantly higher in the Waimea Stream at W-3 and W-7 when compared to W-1, while iron concentrations at W-1 are significantly higher than at W-5 on the Waimea Stream (p-values<0.05). Of the tributaries, Sandstone Stream (S-1) had significantly higher manganese concentrations than W-1 on the Waimea Stream and Longridge Stream (L-4). Iron concentrations at S-1 were also significantly higher than all other sites within the catchment bar N-1, which also had high iron concentrations (p-value < 0.05) (Figure 3-6).

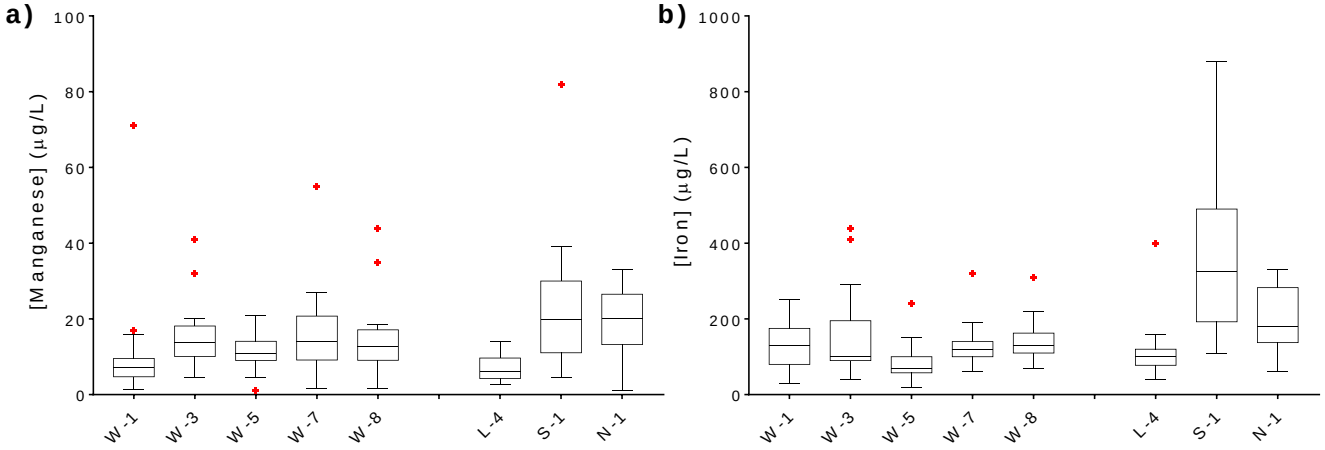

Figure 3-6 Trace metal chemistry of the Waimea catchment. Water chemistry was monitored by Environment Southland for 22 months from September 2012 to June 2014 at different sites along the Waimea Stream (W-1,3,5,7,8), Longridge Stream (L-4), North Peak Stream (N-1) and Sandstone Stream (S-1) (for locations see Figure 3-1) and the dissolved concentration of a) manganese, b) iron were determined monthly. Tukey plots with the median and interquartile range from 22 measurements are displayed. The whiskers represent 1.5 X interquartile range. Outliers are marked by red crosses.

3.2.3. Seasonal variation is surface water chemistry

In this section variation in hydrochemistry between summer and winter is investigated in order to identify the chemical character of base flows and high or flood flows. From this, different end-members contributing to flow were identified.

Broad differences were characterised by comparing the chemical facies and major ion proportions between summer and winter. For this the mean concentration for June to August 2013 were contrasted with the mean concentrations for January to March 2014. These two periods were selected for analysis because they exhibited dry low flow conditions for the summer period, and wet high flow conditions for the winter period. June to August of 2013 recorded a mean flow rate for the Waimea Stream at Mandeville of 5.73 m^3/sec, whereas January to March of 2014 recorded a mean flow for the Waimea Stream at Mandeville of 1.11 m^3/sec.

Major water facies

There was a shift in chemical facie between summer and winter (Figure 3-7). Over summer all sites had HCO_3 type waters. However, over winter there was a shift towards greater Cl and SO_4 dominance at all sites. The hill-fed sites of W-1 and N-1 were more strongly dominated by HCO_3 than the other sites in the Waimea catchment over summer. Over winter there was also a shift towards a greater proportion of Ca throughout the catchment apart from at W-1 and N-1. There was no dominant cation during either summer or winter conditions (Figure 3-7).

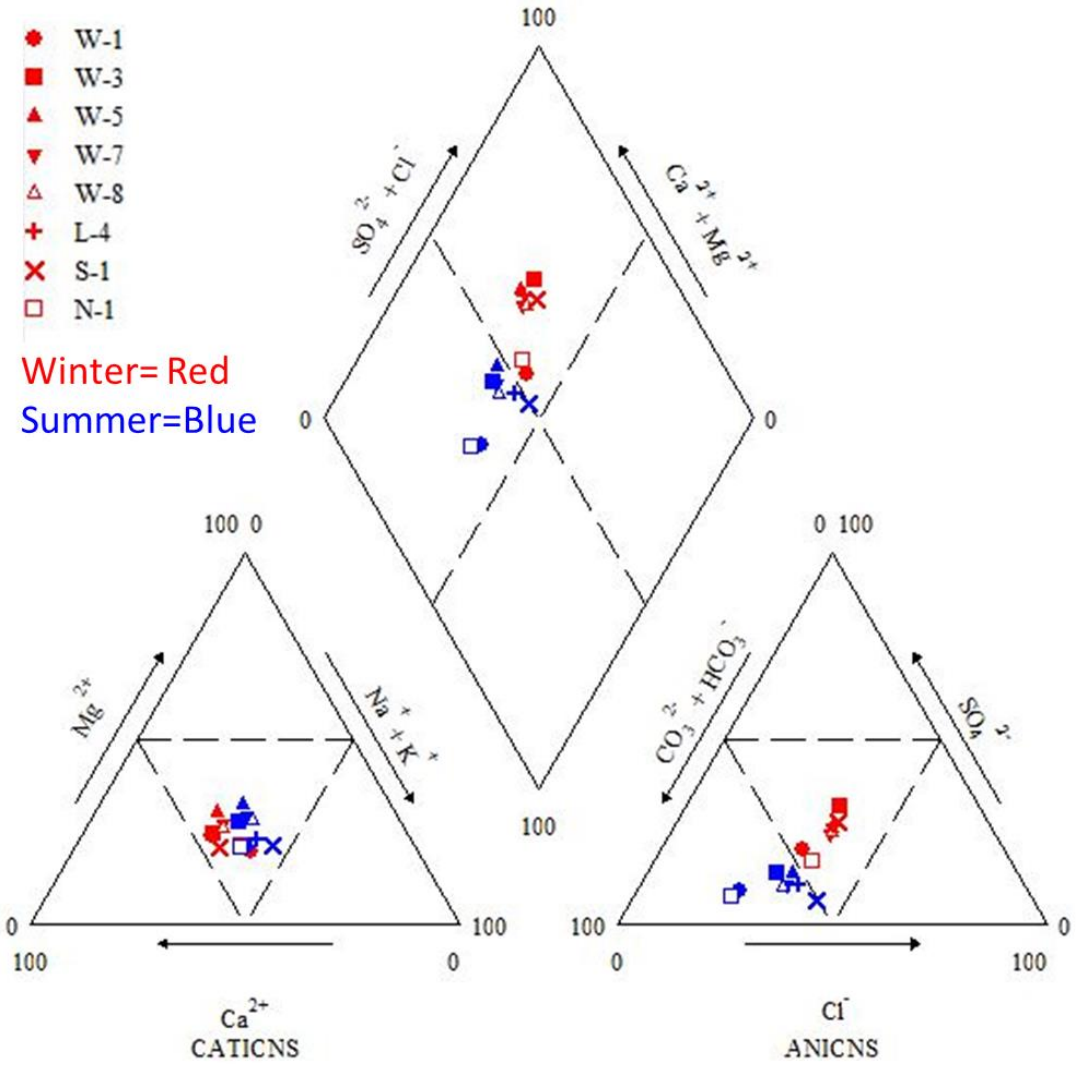

Figure 3-7 Major water facies of the Waimea Catchment. Water chemistry was monitored by Environment Southland for 22 months from September 2012 to June 2014 at different sites along the Waimea Stream (W-1,3,5,7,8), Longridge Stream (L-4), North Peak Stream (N-1) and Sandstone Stream (S-1) (for locations see Figure 3-1). Major water facies are displayed for summer (blue) and winter (red). Summer is the mean of data from January to March 2014, and winter values are a mean of June to August 2013.

Summer and winter major ion proportions

In this section major ion proportions and facies were assessed between summer (mean of data from January to March 2014), and winter (mean of June to August 2013) (Figure 3-8). Data has been converted to meq/L for this analysis.

During summer, all sites were dominated by HCO_3, apart from the lowland tributaries of Longridge Stream (S-1 and L-4) which were equally dominated by Na and HCO_3. During summer all sites monitored had HCO_3-Ca-Na type waters, bar W-5, which had HCO_3-Ca-Mg type waters. During winter all lowland sites became Ca dominated waters, while the hill-fed sites (W-1 and N-1) had equal proportion of HCO_3, Na and Ca. N-1 and W-1 thus had HCO_3-Na-Ca type waters over winter, while all other sites had had HCO_3-Ca-Cl type waters (Figure 3-8).

HCO_3 was the dominant major ion at all sites during summer, however, over winter the HCO_3 proportion dropped significantly, from approximately 30% to 20% at W-1 and N-1, and from approximately 22-25% to 13-15% at all other sites within the catchment (p-value < 0.05). SO_4 was significantly higher over winter, rising at W-1 and N-1, from approximately 3-4% over summer, to approximately 8-9% over winter, and from 3-6% over

summer to 10-14% over winter at all other sites (p-value < 0.05). There was a small but significant increase in K across all sites bar W-1 (p-value < 0.05) over winter. Ca also increased at the lowland sites on the Waimea Stream (W-3,5,7,8) and at N-1 and L-4, from approximately 17-20% over summer, to 23-26% over winter (p-value < 0.05). There was a small but significant decrease in Na proportions at W-5,7,8, L-4 and S-1, between summer and winter. Across these sites the decline in Na was by between 3-5% (p-value < 0.05) (Figure 3-8).

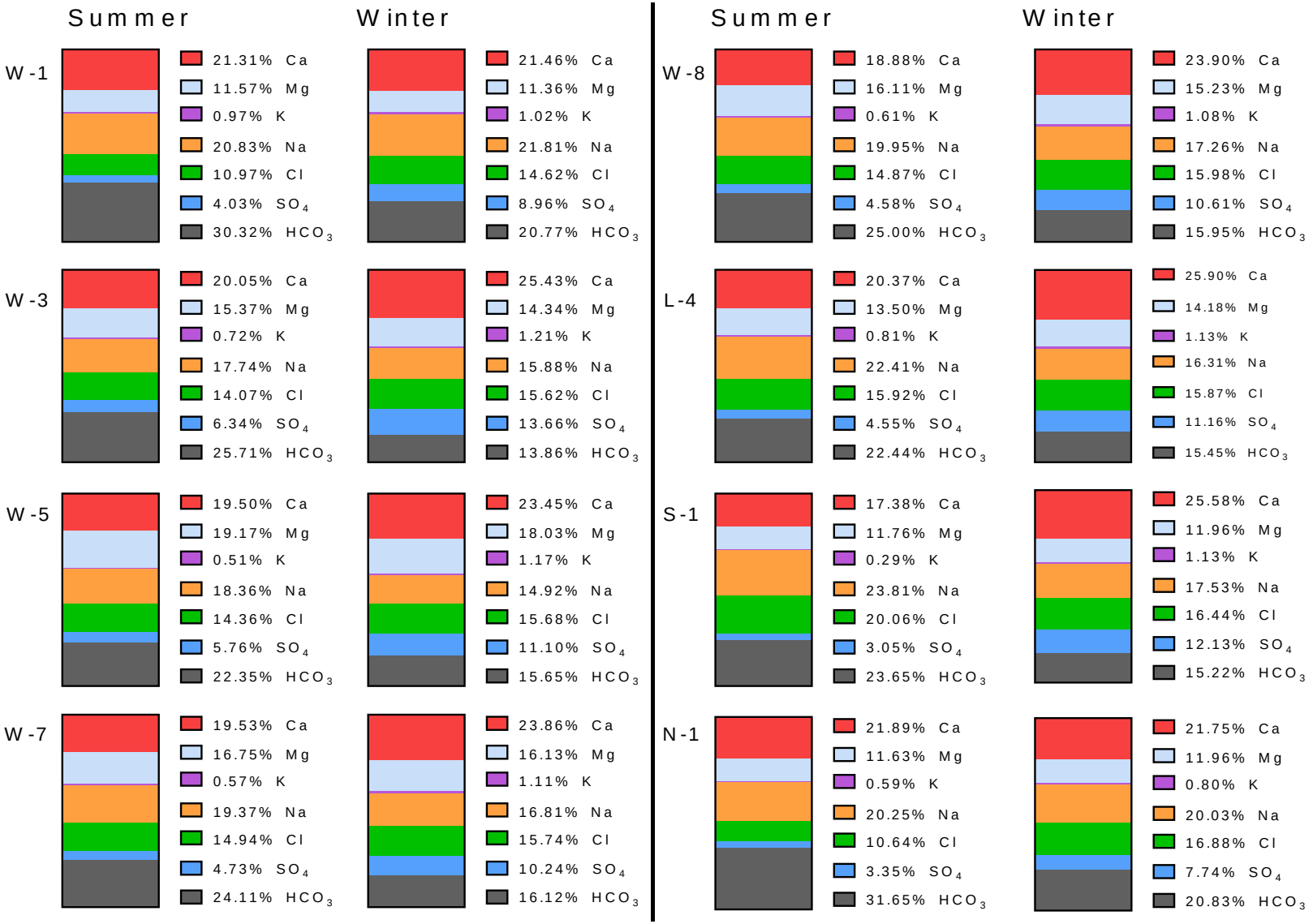

Figure 3-8 Waimea catchment major ion composition during summer and winter. Water chemistry was monitored monthly by Environment Southland for 22 months from September 2012 to June 2014 at different sites along the Waimea Stream (W-1,3,5,7,8), Longridge Stream (L-4), North Peak Stream (N-1) and Sandstone Stream (S-1) (for locations see Figure 3-1) and the concentration of bicarbonate, chloride, sulphate, calcium, sodium, potassium, and magnesium was determined. Here major ion proportions (meq/L) for summer (mean of data from January to March 2014), and winter (mean of June to August 2013) are displayed.

Ion ratios of surface waters and marine aerosols

In this section the ion ratios of the marine aerosols Na, Cl, Mg, SO_4 and Ca were investigated between each site along with any variation between summer and winter. This was done in order to investigate whether there was a significant non-marine aerosol source of ions within the catchment. A significant deviation from the surface water dilution line (SWDL) is indicative of a local source of a solute. Variation between summer and winter was analysed so as to investigate whether any ion ratios deviate greatly from the SWDL during either low flow summer conditions or during high flow winter conditions. This gives an indication of which flow path was likely to be contributing the solute (e.g. overland flow during winter, or groundwater during summer).

The Cl:Na ratio for all surface water samples across the catchment generally fitted the slope of the Na:Cl SWDL, but was offset slightly towards Na (Figure 3-9a). This offset towards Na was more pronounced over summer (Figure 3-9a,e). The Cl:SO_4 ratio did not fit the SWDL, with SO_4 significantly elevated (p-value 0.05) (Figure 3-9b). SO_4 elevation from the SWDL was least pronounced at W-1 and N-2, the two sites that are hill-fed (W-1 and N-1). Both Cl:Mg and Cl:Ca sat off of the SWDL, with significantly higher proportions of Mg and Ca (p-value< 0.05). There was no significant difference between summer and winter for either Cl:Mg or Cl:Ca.

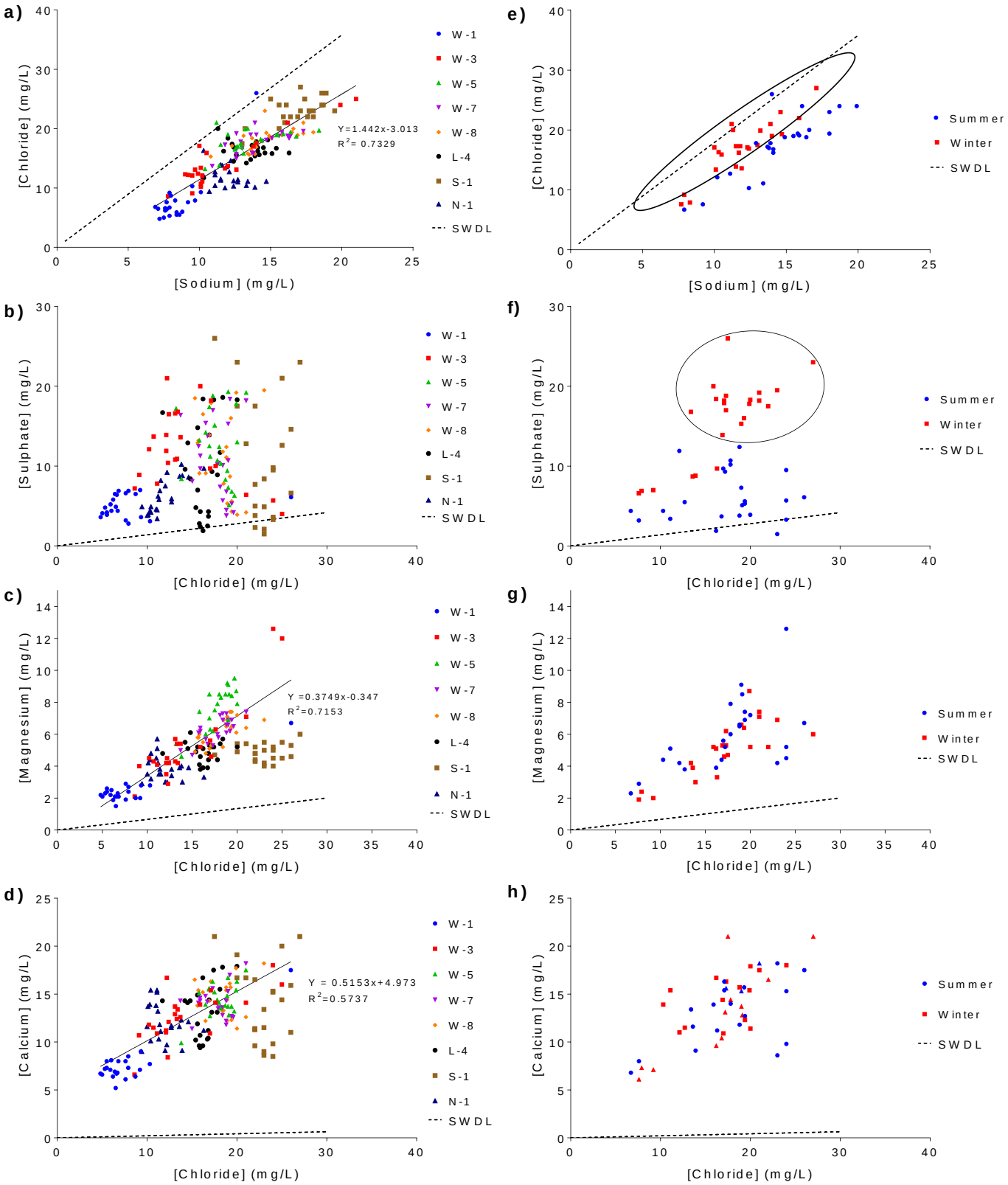

Figure 3-9 Surface water ion ratios of the Waimea Catchment. Water chemistry was monitored by Environment Southland for 22 months from September 2012 to June 2014 at different sites along the Waimea Stream (W-1,3,5,7,8), Longridge Stream (L-4), North Peak Stream (N-1) and Sandstone Stream (S-1) (for locations see Figure 3-1) and the concentration of chloride, sulphate, sodium, and magnesium were determined. Major ion ratios of a,e) chloride and sodium, b,f) sulphate and chloride, c,g) magnesium and chloride, and d,h) calcium and chloride are plotted in relation to their respective sea water dilution lines (SWDL). In a),b),c) and d) the ion ratios are plotted by sampling sites, in d),f),g) and h) ions are plotted by summer and winter. Summer is all data collected during January to March, winter is all data collected during July to August.

Seasonal variation in Na:Cl and SO_4:Cl ratios

The Na:Cl and SO_4:Cl ratios identified as exhibiting variation between summer and winter above were further investigated. The seasonal variation was evident in sites with lowland catchments on the Waimea Plains (W-3,5,7,8, L-4 and S-1), and was not evident at hill-fed sites (N-1 and W-1). There was a clear pattern of an elevated Na:Cl ratio during summer (of approximately 0.8), while during winter the Na:Cl ratio approximated that of marine aerosols (approximately 0.55). The Na:Cl ratio was significantly lower during June, July and August than during the other months monitored (p-value < 0.05). The SO_4:Cl ratio on the other hand was significantly elevated during June to September compared to November to April (p-value < 0.05). During summer the SO_4:Cl ratio approximated that of marine aerosols (0.14) (Brezonik & Arnold, 2011), while during winter it is approximately 1:1 (Figure 3-10).

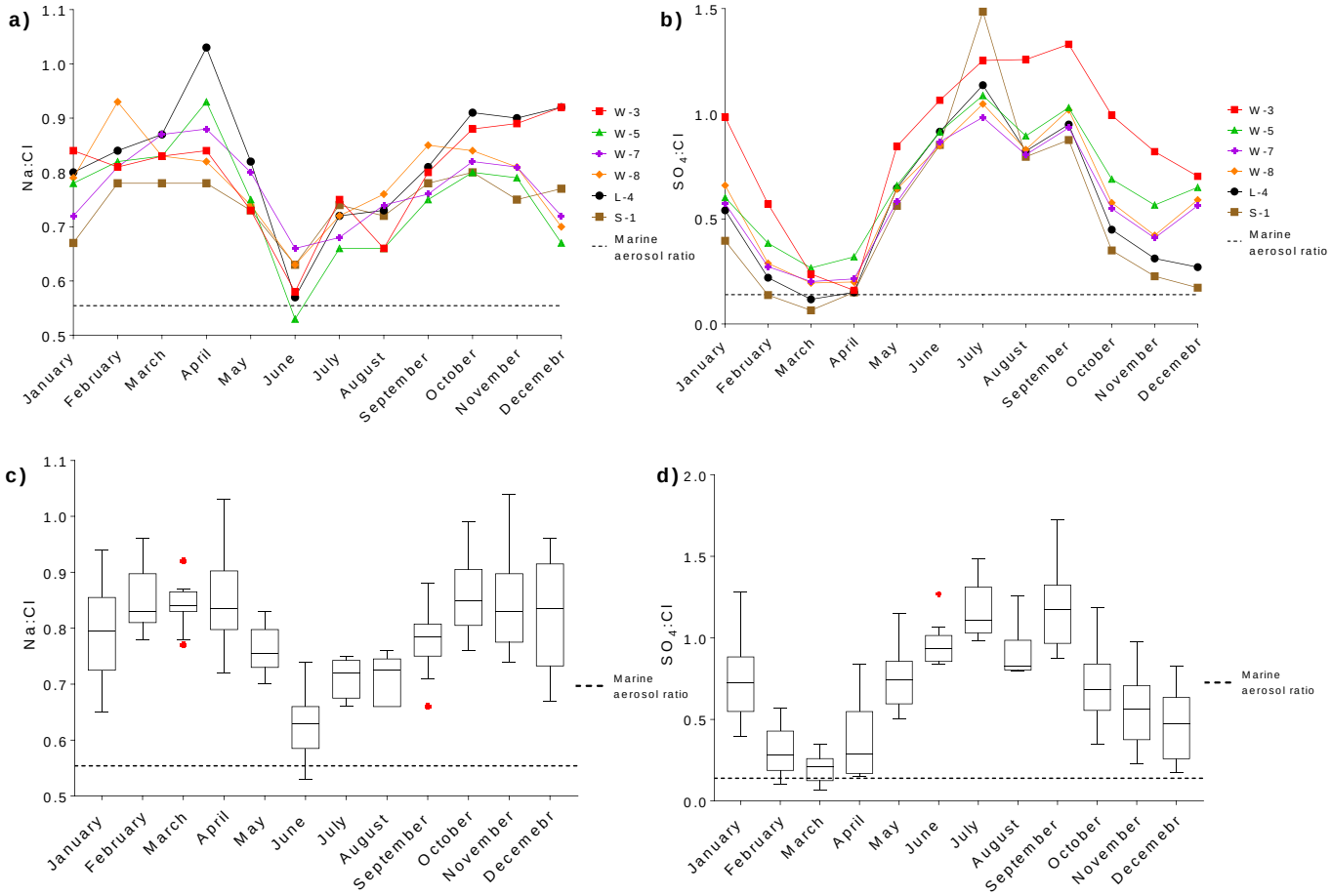

Figure 3-10 Seasonal surface water ion ratios of the Waimea Catchment. Water chemistry was monitored by Environment Southland for 22 months from September 2012 to June 2014 at different sites along the Waimea Stream (W,3,5,7,8), Longridge Stream (L-4) and Sandstone Stream (S-1) (for locations see Figure 3-1) (the hill-fed W-1 and N-1 sites have been excluded here) and the concentration of chloride, sulphate, sodium were determined. The (a,c) sodium:chloride and (b,d) sulphate:chloride ratio from (a,b) January 2013 to December 2013 is displayed along with the (c,d) median and inter quartile range for data collected over the 22 months. The monthly marine aerosol ratio of chloride:sodium and sulphate:chloride is displayed in a) and b) respectively. The whiskers represent 1.5 X interquartile range. Outliers are marked by red crosses.

Monthly hydrochemistry

In this section monthly basic water quality was investigated in order to establish further variance between the different sites and between the different seasons. Firstly, basic water quality was analysed (Figure 3-11), and then monthly chemical changes were investigated (Figure 3-13).

Basic water quality

Water temperature fluctuated steadily between low winter temperatures of approximately 5-7^{o} C and high summer temperatures of approximately 15^{o} C, with temperatures during June to September significantly lower than those during October through to May (p-value < 0.05). Conductivity did not appear to show any statistically significant differences seasonally. There was an apparent spike in conductivity during March 2013 on the Waimea Stream at W-1 and W-3. Levels of pH during July were significantly lower than all other months apart from June and September (p-value < 0.05). This was the month which had by far the highest in-stream flow levels on the day of monitoring (Figure 3-3 and Figure 3-12a). Dissolved oxygen concentrations were significantly lower during March than July (p-value < 0.05). The variation in dissolved oxygen recorded during June and July was significantly less than during October to May, with standard deviations of approximately <0.6, compared to >1.1 (Figure 3-11 and Figure 3-12).

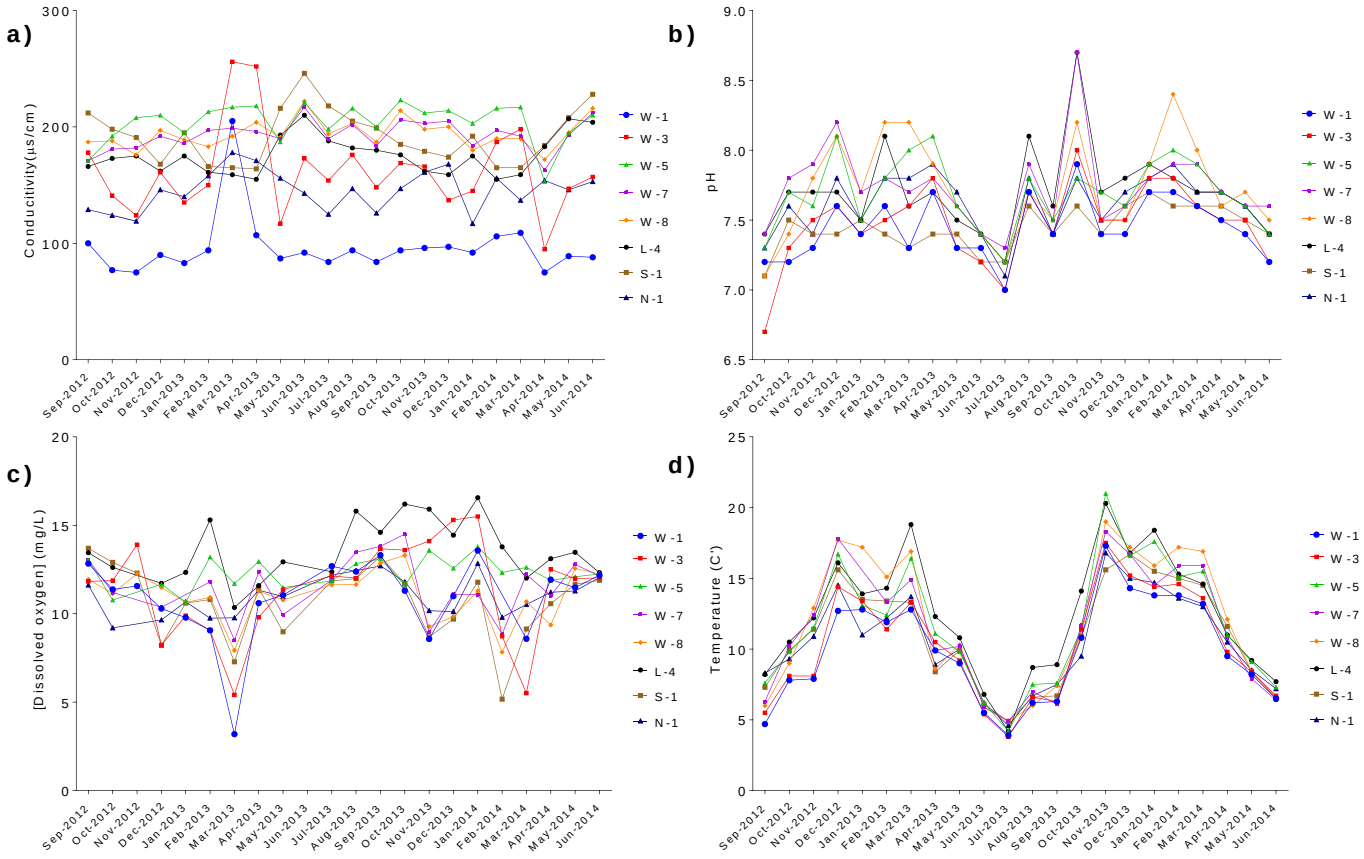

Figure 3-11 Monthly water quality of the Waimea catchment. Water quality was monitored monthly by Environment Southland for 22 months from September 2012 to June 2014 at different sites along the Waimea Stream (W-1,3,5,7,8), Longridge Stream (L-4), North Peak Stream (N-1) and Sandstone Stream (S-1) (for locations see Figure 3-1) and the a) conductivity, b) pH) c) dissolved oxygen, and d) temperature was determined.

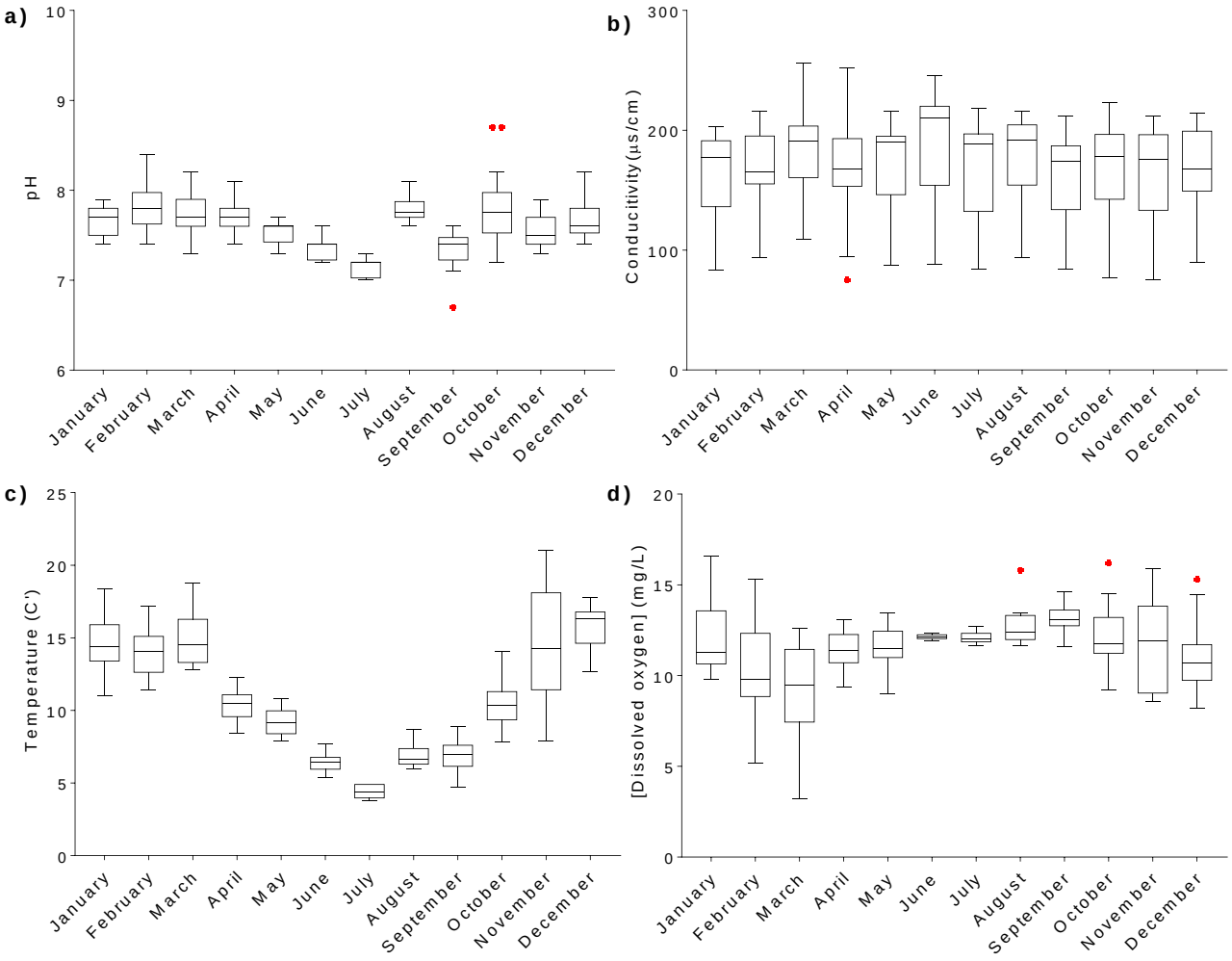

Figure 3-12 Monthly basic water quality of the Waimea catchment. Water quality was monitored by Environment Southland for 22 months from September 2012 to June 2014 at different sites along the Waimea Stream (W-1,3,5,7,8), Longridge Stream (L-4), North Peak Stream (N-1) and Sandstone Stream (S-1) (for locations see Figure 3-1) and the a) pH, b) dissolved oxygen as percentage saturation, c) temperature and d) conductivity was determined. Here Tukey plots of data range for each month with the median and interquartile range are displayed. The whiskers represent 1.5 X interquartile range. Outliers are marked by red crosses.

Major ions

HCO_3 concentrations were significantly lower during May to September compared to November to April (p-value < 0.05), with July having the lowest median concentration (Figure 3-14c). Na concentrations were significantly lower during July than February and March (Figure 3-14g) (p-value < 0.05). Ca, K, and SO_4 were all significantly higher over the winter months at all sites within the catchment except for W-1 and N-1 (p-value < 0.05) (Figure 3-13 and Figure 3-14).

At W-1 and W-3 there was a large spike in Cl, HCO_3, Ca, Mg and Na during the months of March and April 2013. No significant seasonal variation in Cl or Mg was observed.

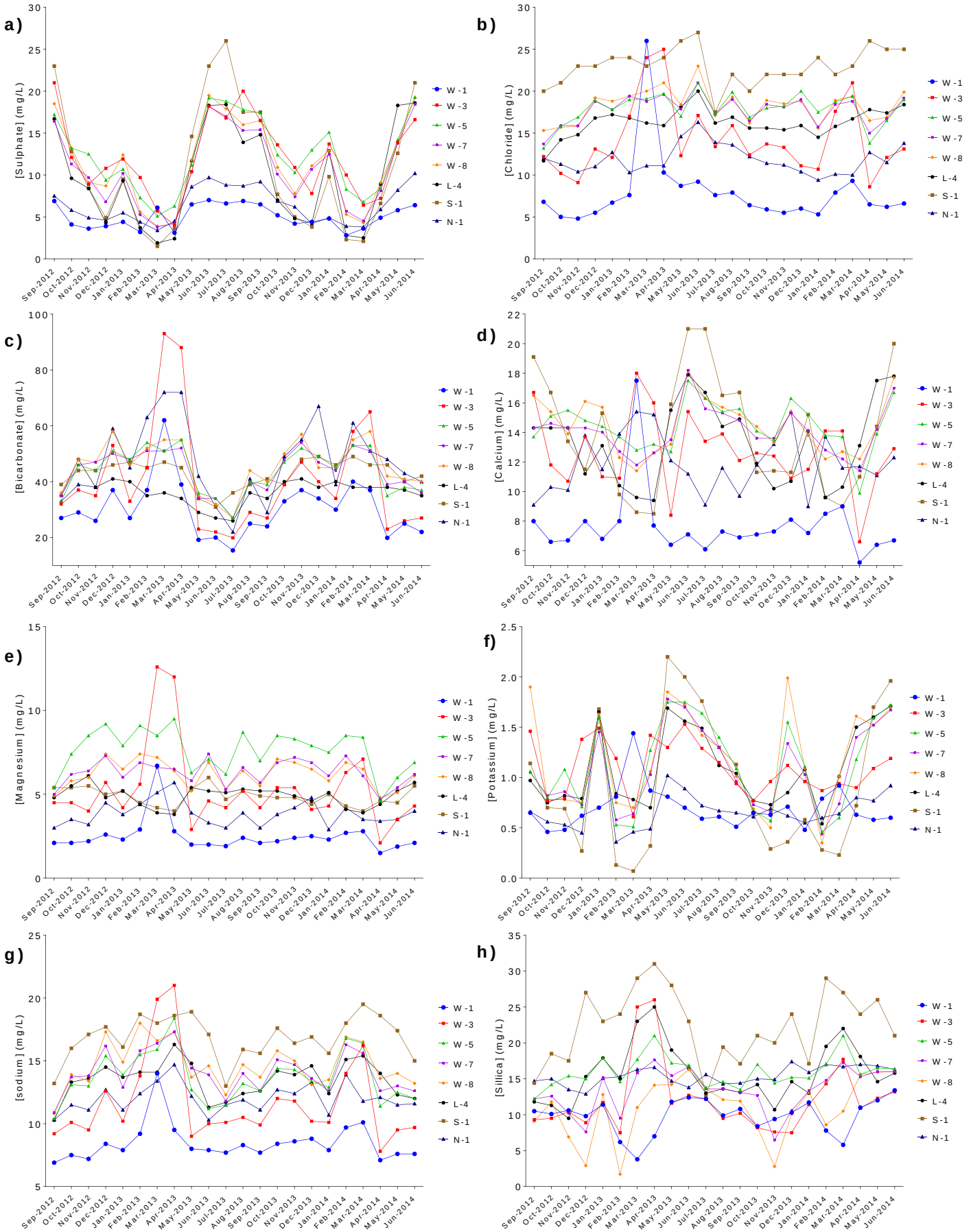

Figure 3-13 Monthly major ion chemistry of the Waimea catchment. Water chemistry was monitored by Environment Southland for 22 months from September 2012 to June 2014 at different sites along the Waimea Stream (W-1,3,5,7,8), Longridge Stream (L-4), North Peak Stream (N-1) and Sandstone Stream (S-1) (for locations see Figure 3-1) and the concentration of a) sulphate, b) chloride, c) bicarbonate d) calcium, e) magnesium, f) potassium, g) sodium, and h) silica were determined.

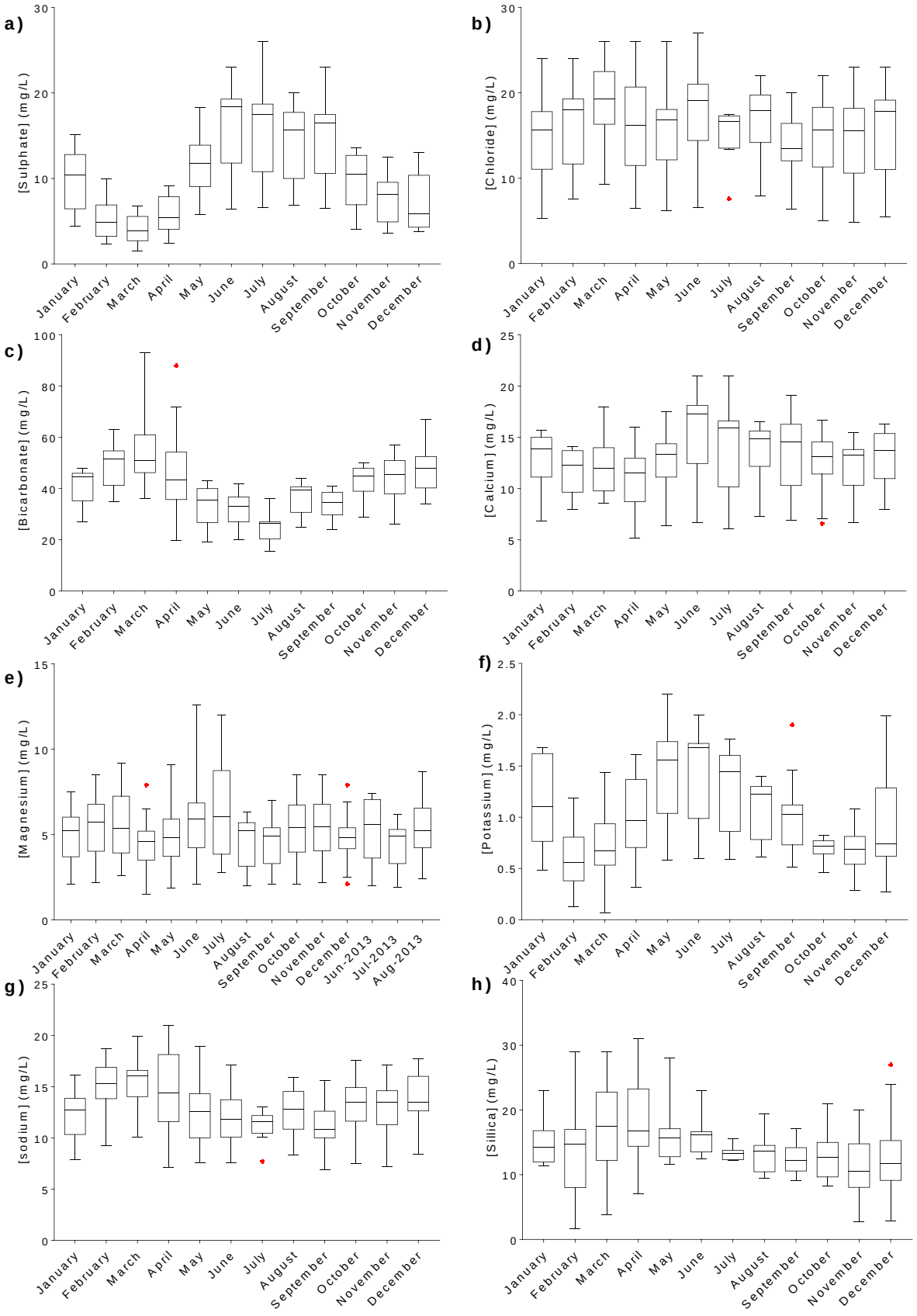

Figure 3-14 Monthly major ion chemistry of the Waimea catchment. Water chemistry was monitored by Environment Southland for 22 months from September 2012 to June 2014 at different sites along the Waimea Stream (W-1,3,5,7,8), Longridge Stream (L-4), North Peak Stream (N-1) and Sandstone Stream (S-1) (for locations see Figure 3-1) and the concentration of a) sulphate, b) chloride, c) bicarbonate d) calcium, e) magnesium, f) potassium, g) sodium, and h) silica were determined.. Here Tukey plots of data range for each month with the median and interquartile range are displayed. The whiskers represent 1.5 X interquartile range. Outliers are marked by red crosses.

Trace metals

Concentrations of Fe were significantly elevated during January relative to July (Figure 3-16). Concentrations of Mn spiked during January to March 2013 at W-1 and W-2, and during November and December 2013 at W-7 and S-1. Manganese concentrations during January and February were not significantly different from those in June to August (Figure 3-15 and Figure 3-16).

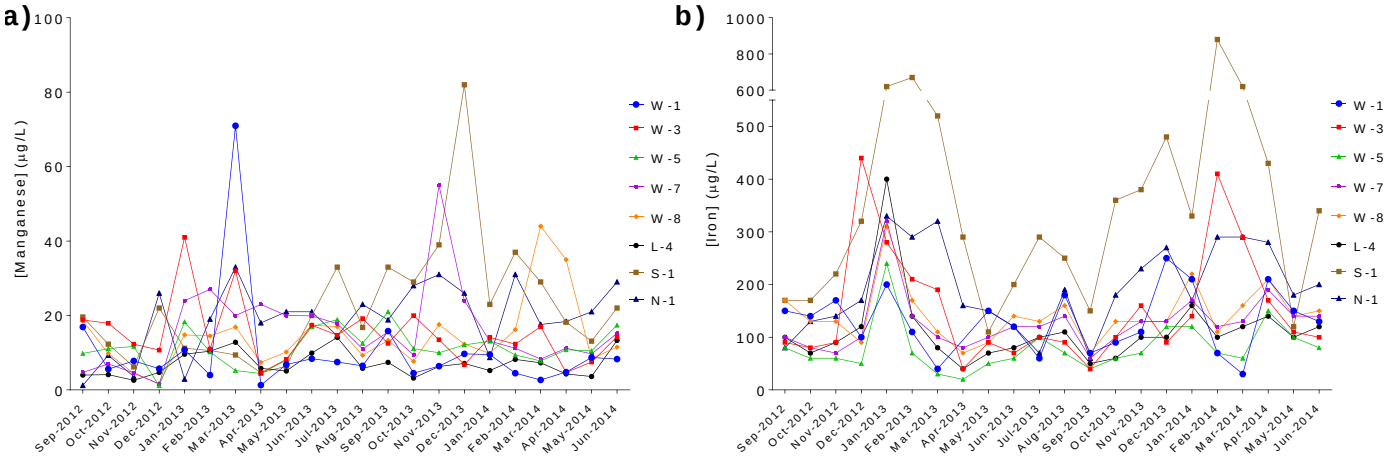

Figure 3-15 Monthly trace metal chemistry of the Waimea catchment. Water chemistry was monitored by Environment Southland for 22 months from September 2012 to June 2014 at different sites along the Waimea Stream (W-1,3,5,7,8), Longridge Stream (L-4), North Peak Stream (N-1) and Sandstone Stream (S-1) (for locations see Figure 3-1) and the concentration of a) manganese, b) iron were determined.

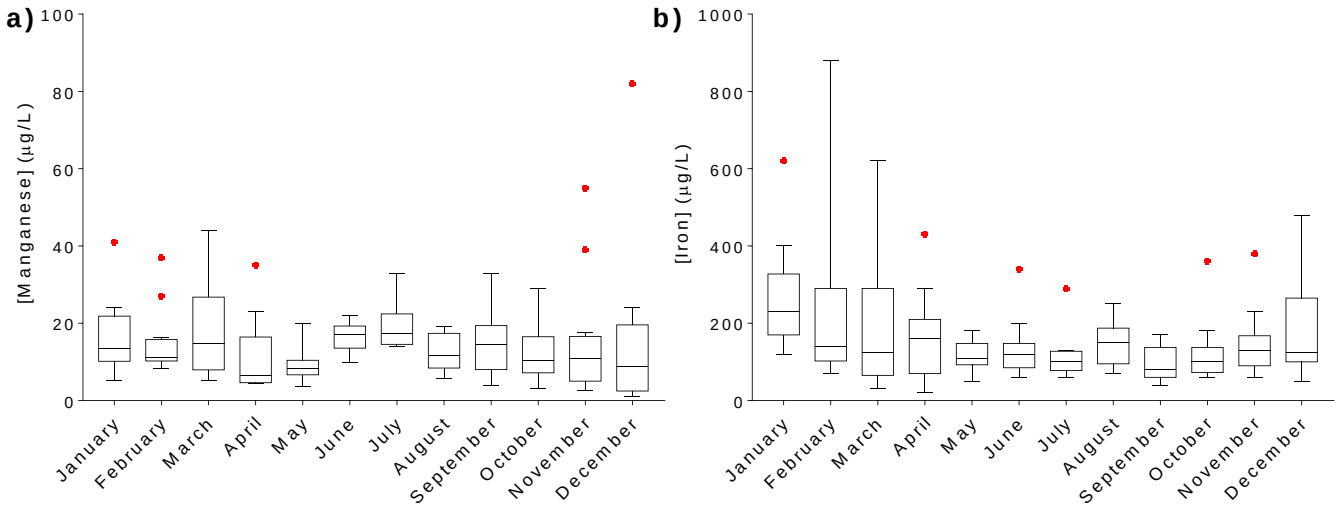

Figure 3-16 Monthly trace metal chemistry of the Waimea catchment. Water chemistry was monitored by Environment Southland for 22 months from September 2012 to June 2014 at different sites along the Waimea Stream (W-1,3,5,7,8), Longridge Stream (L-4), North Peak Stream (N-1) and Sandstone Stream (S-1) (for locations see Figure 3-1) and the concentration of a) manganese and b) iron was determined. Here Tukey plots of data range for each month with the median and interquartile range are displayed. The whiskers represent 1.5 X interquartile range. Outliers are marked by red crosses.

3.2.4. Surface water chemistry and flow

In this section, in-stream flow was compared to a number of solutes to establish whether conditions directly correlate with solute concentrations. Flow data was taken from the Environment Southland's flow gauge on the Waimea Stream at Mandeville. Flow values are the mean flow recorded at Mandeville on the

day on which samples were collected. It has been assumed that the relative flow at the other sampling sites within the Waimea Catchment will approximate that of the flow of the Waimea at Mandeville.

SO_4 concentrations correlated strongly with flow at all sites within the Waimea catchment (R^2=0.6969) except for at W-1 and N-1 where the correlation was weaker (R^2=0.3868) (Figure 3-17a,b).

HCO_3 concentrations correlated negatively with flow at all sites bar L-4 and S-1. An overall analysis of the relationship between HCO_3 and flow at all sites, bar L-4 and S-1 using spearman's rank correlation coefficient, yielded an r value of 0.62 (p-value < 0.05). Linear regression analysis for each site on the Waimea Stream yielded R^2 values between 0.47 and 0.57, and for N-1 an R^2 of 0.74 (Figure 3-17c).

Na also correlated negatively with flow. An overall analysis of the relationship between Na and flow at all sites using spearman's rank correlation coefficient yielded an r value of 0.61 (p-value < 0.05). The strength of the correlation between Na and flow differed between sites, with linear regression analysis yielding an R^2 between 0.64 and 0.82 for all sites bar W-1 and W-2. For these two sites the correlation was less significant with R^2 values of 0.46 and 0.52 respectively (Figure 3-17e).

Silica did not correlate with flow in the lower Waimea, however it did correlate negatively with flow at S-1 (R^2=0.7570) and W-5 (R^2=0.4404). At W-1 the reverse relationship was true, with silica correlating positively with flow (R^2=0.5640) (Figure 3-17g,h).

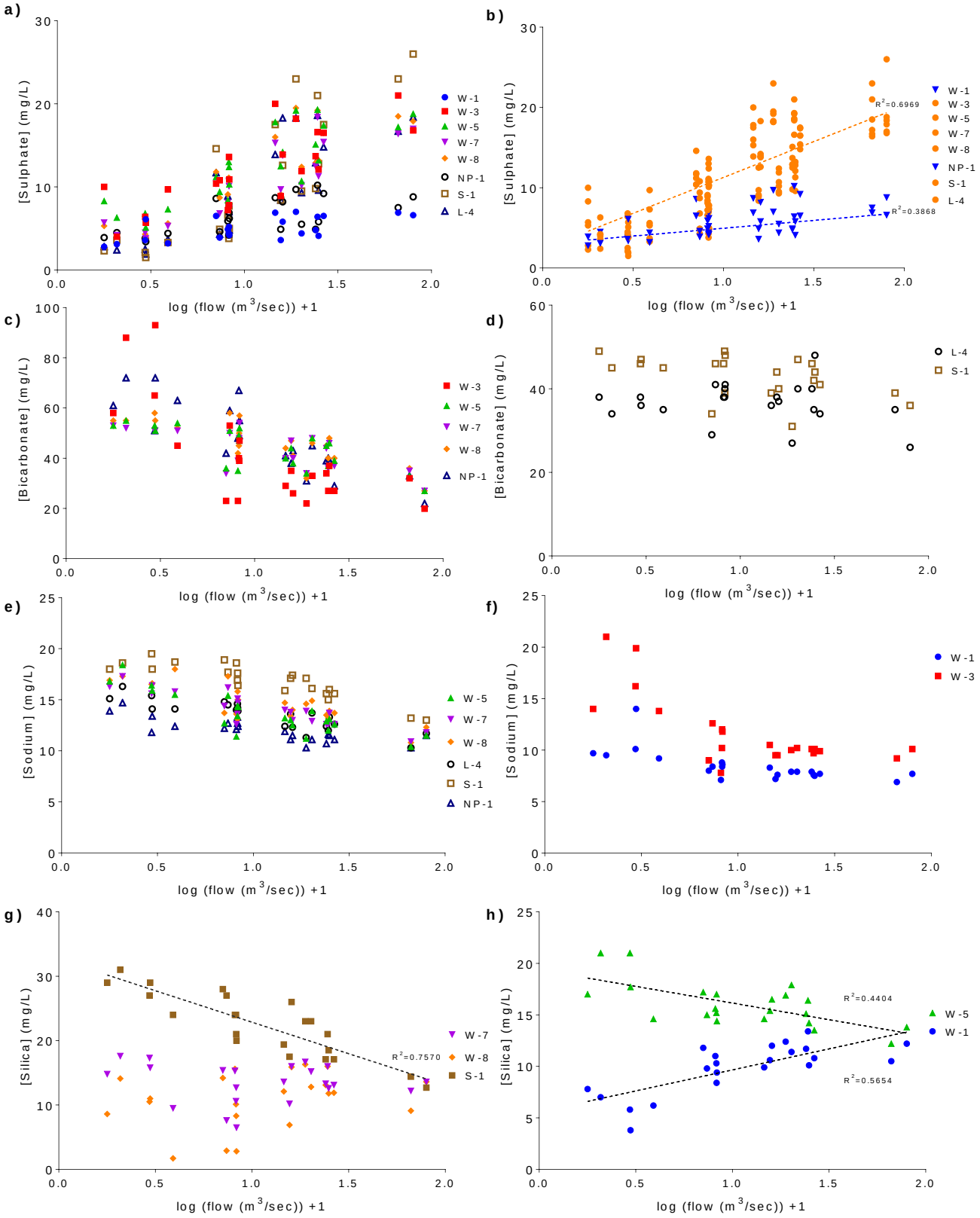

Figure 3-17 Surface water chemistry and in-stream flow. Water chemistry was monitored by Environment Southland for 22 months from September 2012 to June 2014 at different sites along the Waimea Stream (W-1,3,5,7,8), Longridge Stream (L-4), North Peak Stream (N-1) and Sandstone Stream (S-1) (for locations see Figure 3-1) and the concentration of a,b) sulphate, c,d) bicarbonate, e,f) sodium and g,h) silica was determined. Flow readings avlre the mean recorded flow of the Waimea Stream at Mandeville on the day of sampling and have been log transformed. Flow reading were recorded by Environment Southland (D. May, personal communication, December 15 2015). Linear regressions have been carried in b) for (W-3,5,7,8,L-4,S-4) and (W-1,N-1), in g) for (S-1) and in h) for (W-5) and (W-1). Spearman rank correlation co-efficient have been carried out for all data points in c) r=-0.62 and e) r=-0.61 (p-value < 0.05).

3.3. Groundwater chemistry

In this section the chemistry of groundwater across the Waimea Plains was analysed. Groundwater chemistry has been characterised from several bores across the Waimea Plains (Figure 3-18). The amount of data collected from each bore varies, with some bores only having a single set of data for some parameters. E44/0036 and E44/0008 both have had a significant amount of data collected by Environment Southland, with data being collected every 3 to 5 months for the past 15 years for both, including a full suite a major ion concentrations.

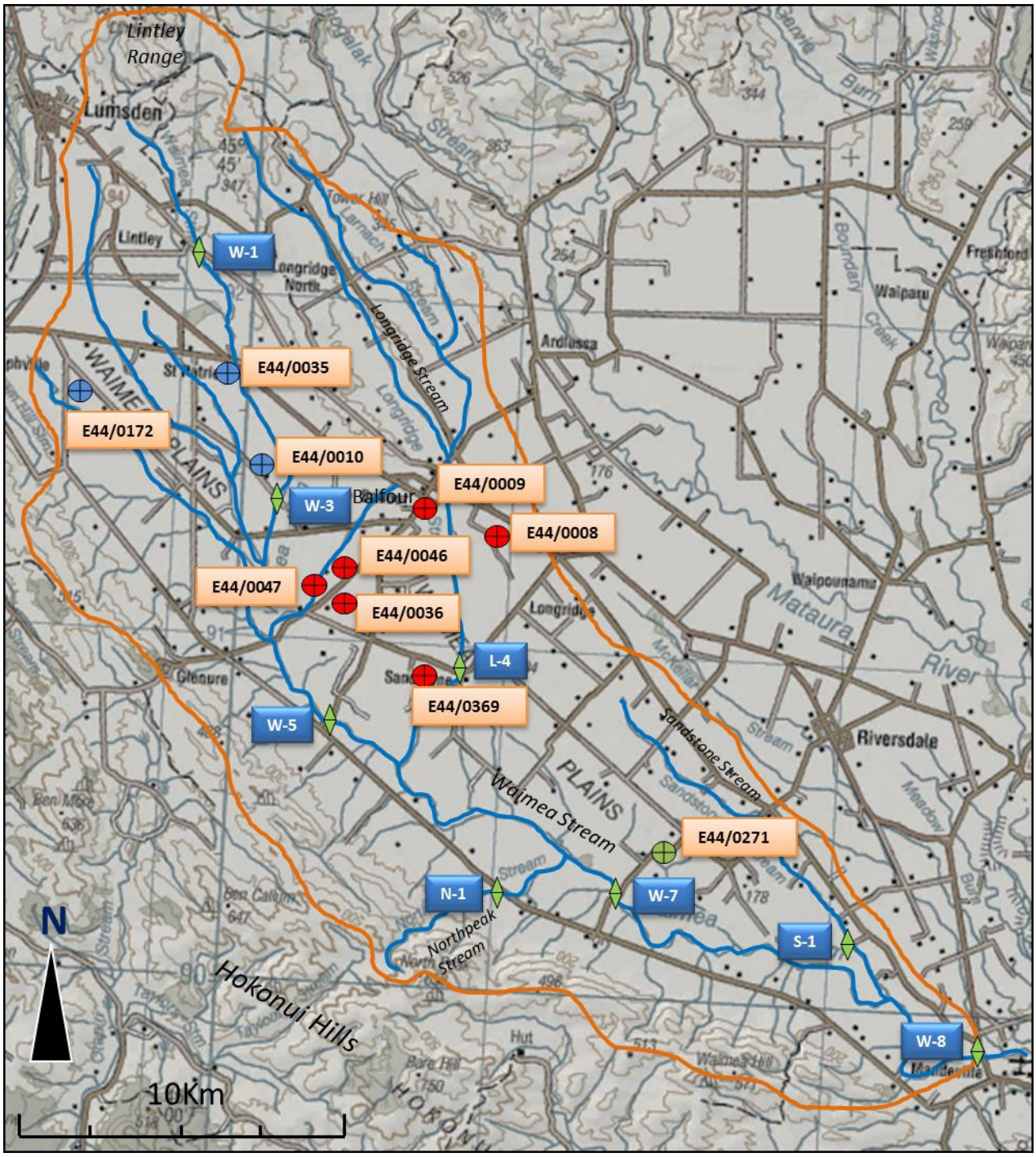

Figure 3-18 Environment Southland surface water monitoring sites and groundwater monitoring bores. Surface water monitoring sites on the Waimea Stream (W-1,3,5,7,8), Longridge Stream (L-4), North Peak Stream (N-1) and Sandstones Stream (S-1) are displayed (green diamonds). Crosshairs represent groundwater bores and are in three groups (blue= upper Waimea, red= Balfour nitrate hotspot, green= lower Waimea). The orange line is the approximate catchment of the Waimea Stream.

3.3.1. Major ion chemistry

In this section the chemistry of groundwater across the Waimea Plains is characterised. Firstly, spatial chemical facies were investigated with a piper plot. Secondly, the ion ratios of Na:Cl and SO4:Cl were investigated. Thirdly, temporal trends in chemistry were studied on both a long term scale, and on a seasonal level. The aim of this section was to identify the chemical character of the Waimea Plains groundwater end-member.

Groundwater chemical facies

Water type has been analysed using a piper plot (Figure 3-19), with groundwater being grouped in to three groups, those that lie above the Balfour nitrate hotspot in the upper Waimea Plains (blue symbols), those that lie within the Balfour nitrate hotspot (red symbols), and those that lie in the lower Waimea Plains (green symbols) (for map see Figure 3-18).

Groundwater from bores E44/0035 and E44/0010, which lie in the upper Waimea Plains above the nitrate hotspot, could be characterised as HCO_3 type waters. All other groundwater analysed were Cl dominated waters, and were either within the Balfour nitrate hotspot or down-gradient of it. The exception to this was E44-0172, which was dominated by Cl and is located in the upper Waimea Plains (Figure 3-19).

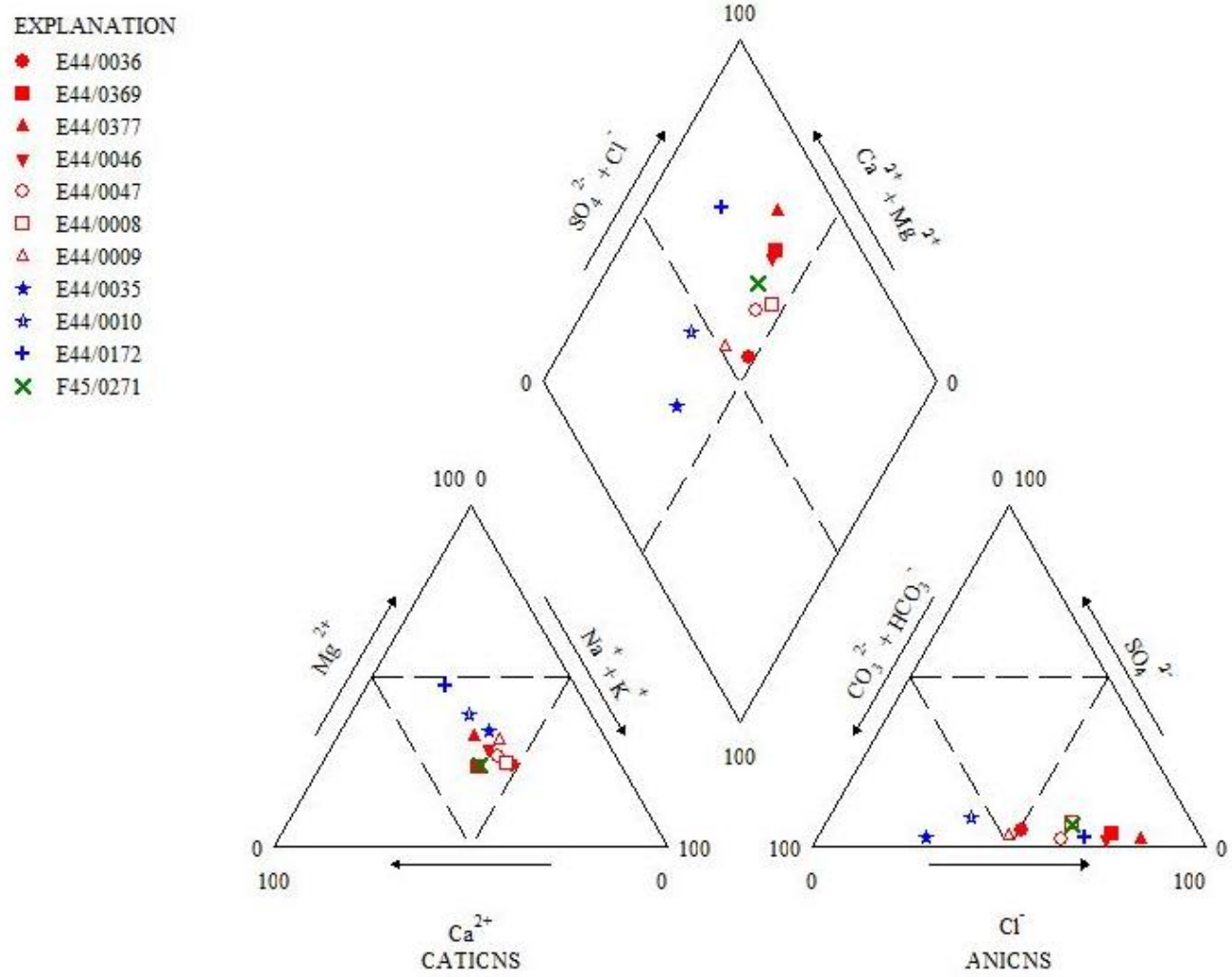

Figure 3-19 Major water facies of the Waimea Plains groundwater. The water chemistry of groundwater has been monitored by Environment Southland for various bores across the Waimea Plains between 2001 and 2015 (for locations see Figure 3-18. The data used here is a mean of major ion data collected by Environment Southland for each site to 2015. Bores have been divided into three groups, those that lie within the Balfour nitrate hotspot (red), those that lie in the upper Waimea Plains outside of the Balfour nitrate hotspot (blue), and those that lie outside of the nitrate hotspot in the lower Waimea Plains (green).

Groundwater ion ratios

Groundwater had a Na:Cl ratio significantly above that of marine aerosols, with a median ratio 0.94 for all groundwater sampled by Environment Southland. This contrasts to the marine aerosol ratio of 0.55. The median SO_4:Cl ratio of Waimea Plains groundwater was 0.12, which is below the marine aerosol ratio of 0.14 (Figure 3-20).

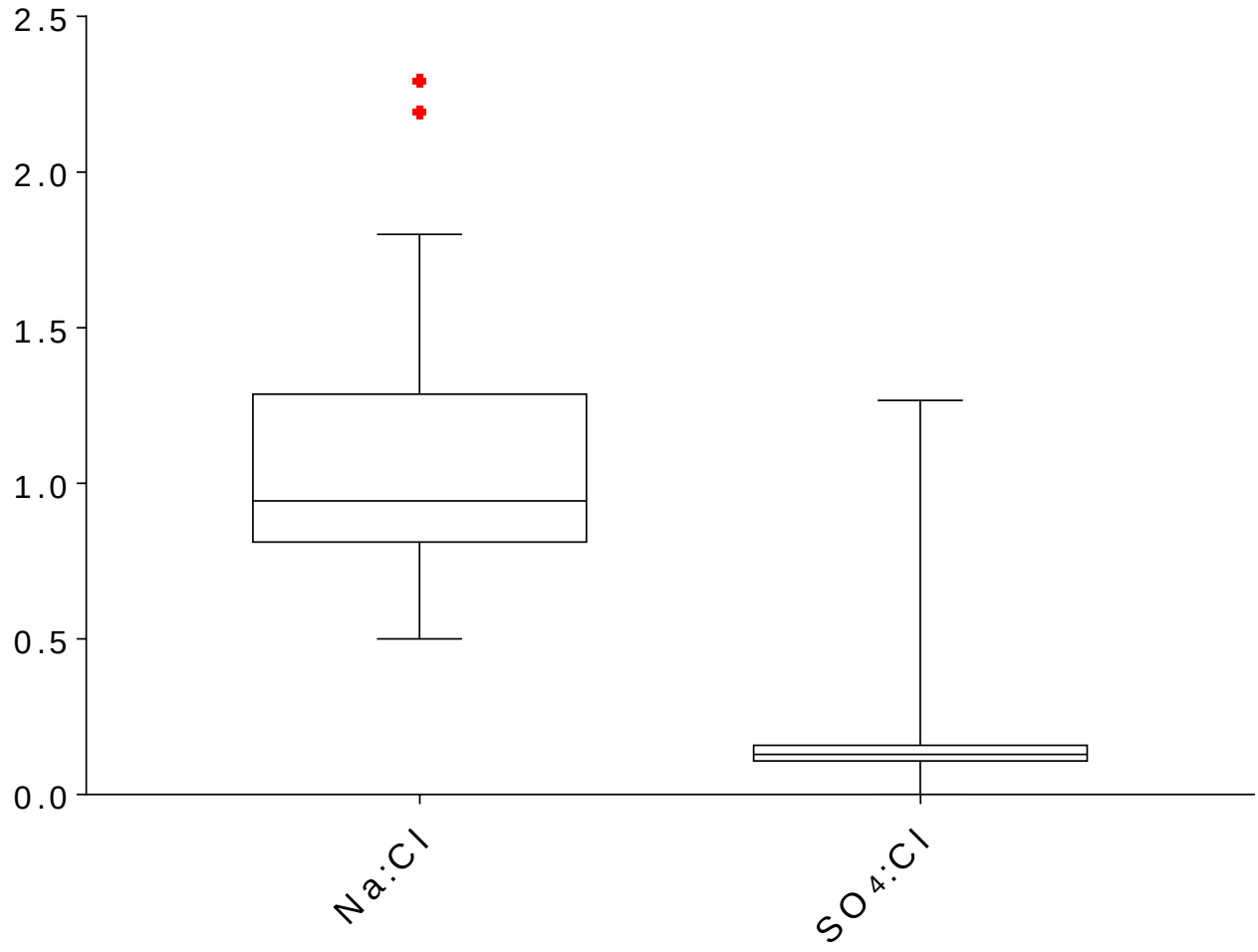

Figure 3-20 Groundwater ion ratios of Na:Cl and SO4:Cl. The water chemistry of groundwater has been monitored by Environment Southland for various bores across the Waimea Plains between 2001 and 2015 (for locations see Figure 3 18). Tukey plots with the median and interquartile range from all data collected over this period are displayed. The whiskers represent 1.5 X interquartile range. Outliers are marked by red crosses.

Trends in groundwater chemistry with time

Bore E44/0036 and E44/0008 have had a full suite of hydrochemical data collected between 2000 and 2015. Both lie within the Balfour nitrate hotspot (for map see Figure 3-18). Changes in major ion concentrations were assessed. There was an increasing trend in a number of major ions in the groundwater from these two bores (Figure 3-21). Bore E44/0036 showed a positive trend in Cl, Na, and Mg and over the period 2001 to 2015. On average Cl has increased by 0.30 mg/L per year, Na by 0.18 mg/L, Mg by 0.09 mg/L, and Ca by 0.16 mg/L. Bore E44/0008 had increasing concentrations in SO_4, HCO_3, Cl, Na, Mg and Ca. On average SO_4 has increased by 0.07 mg/L per year, HCO_3 by 0.24 mg/L, Cl by 0.33 mg/L, Na by 0.22 mg/L, Mg by 0.08 mg/L and Ca by 0.1 mg/L per year. These trends were significant (p-value < 0.05) when analysed using spearman's rank correlation coefficient, with both bores showing a particularly strong trend of increasing Cl concentrations (Spearman's r-value>0.9) (Figure 3-21 and Table 3-1).

Table 3-1 Trend analysis of major ion concentrations in groundwater. Spearman rank correlation coefficient values for Bore E44/0036 and Bore/0008 as a measure of trends in major ion concentration in groundwater. A positive value indicates a significant increasing trend with time, negative values a decreasing trend. Blanks indicate no significant correlation. All values given have a p-value < 0.05.

Bore	SO_4	HCO_3	Cl	Na	K	Mg	Ca
E44/0036	-	-	+0.9321	+0.7639	-	+0.7699	+0.8097
E44/0008	+0.8059	+0.6848	+0.8962	+0.9076	-	+0.8941	+0.8735

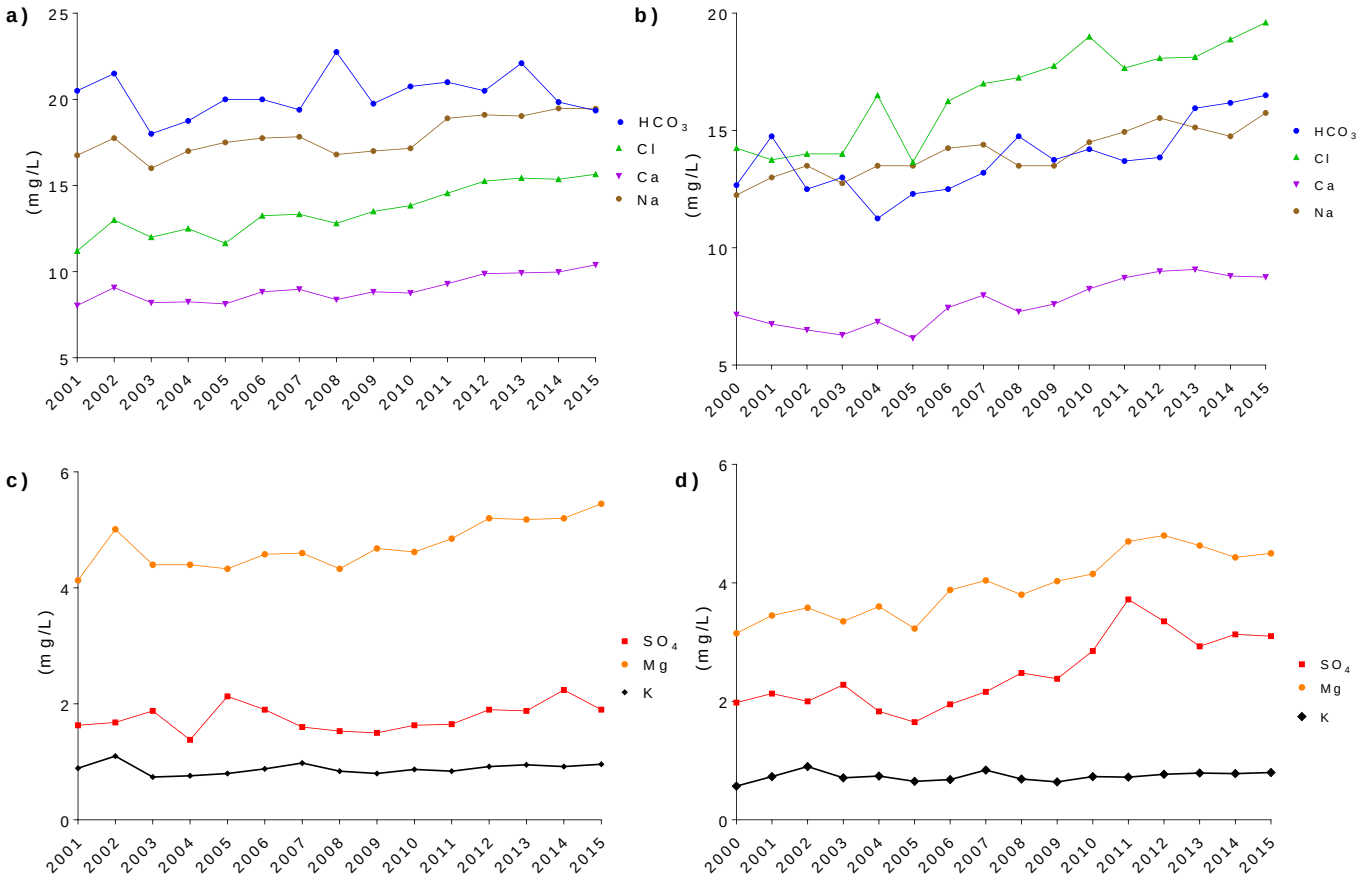

Figure 3-21 Groundwater major ion trends. Trends in major ions of bore a,c) E44/0036 and b,d) E44/0008. Environment Southland has monitored the chemistry of E44/0036 and E44/0008 between 2001-2015 and 2000-2015 respectively. The concentration of a,b) bicarbonate, chloride, sodium, calcium, c,d) sulphate, potassium, and magnesium has been determined annually. Yearly concentrations are an average of multiple measurements where multiple data points exited. Both bore's lie within the 'Balfour nitrate hotspot' (for map see Figure 3-18).

Seasonal trends in groundwater chemistry

Seasonal differences in ground water chemistry between summer and winter were investigated. Bores E44/0036 and E44/0008 have been investigated as each has sufficient data for this analysis to be undertaken. Summer includes all data collected in January, February or March, while winter includes all data collected in June, July or August between 2000 and 2015. Data has been displayed using box plots. There was no statistically significant difference in chemistry between summer and winter for any solute in either bore as determined by a t-test and ANOVA (p-value > 0.05) (Figure 3-22).

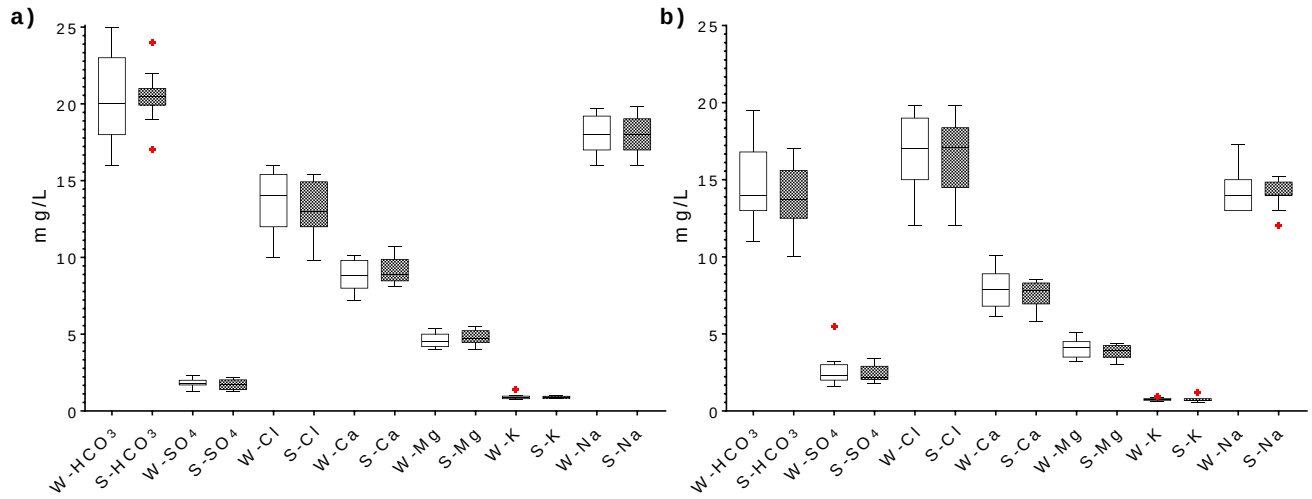

Figure 3-22 Seasonal groundwater major ion chemistry. Environment Southland has monitored the chemistry of E44/0036 and E44/0008 between 2001-2015 and 2000-2015 respectively. The concentration of bicarbonate, chloride, sodium, calcium, sulphate, potassium, and magnesium has been determined annually through multiple measurements. Here samples taken in January to March (summer(S)-shaded boxes) have been compared to samples taken in June to August (winter(W)-clear boxes) for a) bore E44/00336 and b) E44/0008. No significant difference was found between summer and winter for any major ions (p-value > 0.05).

3.4. Nutrient chemistry

In the following, nutrient concentrations were characterised for both surface and groundwater. For groundwater, trends in DRP and nitrate concentrations are investigated from data collected between 2000 and 2015. For surface water, nutrient concentrations were investigated both spatially and temporally. Firstly, differences in nutrient concentration between different sites were analysed. Secondly, monthly nitrate concentrations were displayed for 2006, 2007, 2008 and 2013 to illustrate both seasonal changes and variation in nitrate dynamics between different years. Thirdly, nitrate concentrations between summer and winter were examined between different sites. Fourthly, nitrate concentrations were related to in-stream flow for each monitoring site.

3.4.1. Groundwater nutrients

For nitrate, three bores from within the Balfour nitrate hotspot (E44/0046, E44/0047 and R44/0036), and two from the upper Waimea Catchment (E44/0035 and E44/0010) have been investigated. These have been chosen as each has sufficient data collected to establish any trends that may exist. For DRP, only two bores have sufficient data to investigate any possible trend, E44/0008 and E44/0036 (for map see Figure 3-18).

Nitrate

Groundwater nitrate concentrations from bores E44/0046, E44/0047 and R44/0036 all showed an increasing trend in nitrate concentrations between 2005 and 2015. These three bores are all located near Balfour, within the 'nitrate hotspot'. E44/0036 has had an average increase of 0.31 mg/L per year of NO_3-N between 2005 and 2015, rising from 10.44 mg/L in 2005 to 13.50 mg/L in 2015. By 2007 all three bores had groundwater nitrate concentrations above the maximum allowable value for human drinking water, as set by the Ministry of Health, of 11.3 mg/L NO_3-N (Ministry of Health, 2008). By 2013 the nitrate concentration in groundwater from E44/0046 had reached 24.0 mg/L from 20.0 mg/L in 2005, a rise of 0.5 mg/L per year. Bore E44/0035 and E44/0010 near St Patricks, which is in the upper part of the catchment and outside of the 'Balfour nitrate hotspot', had significantly lower nitrate concentrations, with nitrate concentrations near or below 1.0 mg/L, with no trend towards higher nitrate concentrations apparent (Figure 3-23).

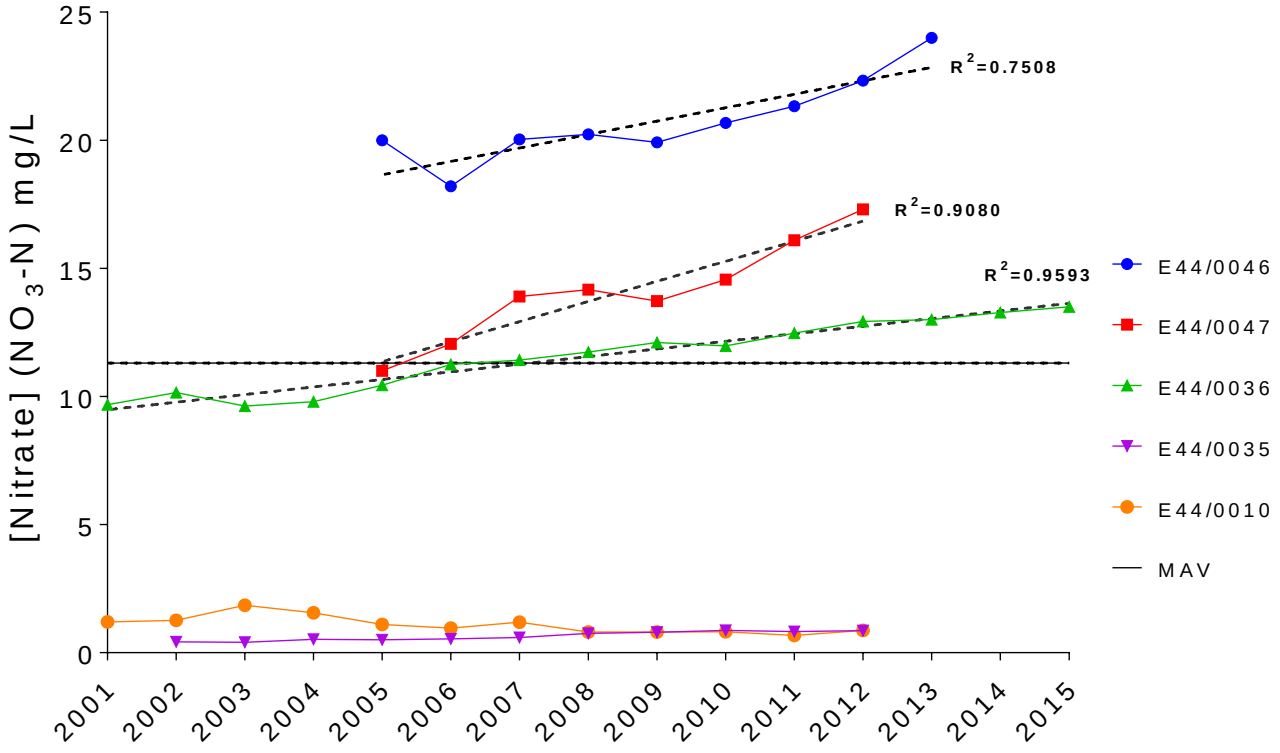

Figure 3-23 Temporal trends in groundwater Nitrate on the Waimea plains. E44/0046, E44/0047, E44/0036, E44/0035 and E44/0010 were monitored for nitrate concentrations annually by Environment Southland. E44/0046, E44/0047 and E44/0036 all lie within the 'Balfour nitrate hotspot'. E44/0035 and E44/0010 lie outside of the Balfour hotspot, near Saint Patricks. Annual nitrate concentrations between 2001 and 2015 for each bore are displayed. MAV is the maximum allowable value of 11.3 mg/L NO_3-N for human drinking water, as set by the Ministry of Health (Ministry of Health, 2008).

Dissolved reactive phosphorus

Dissolved reactive phosphorus (DRP) concentrations in groundwater from bore E44/0036 were significantly higher than from E44/0008, with the former ranging from 20.0 µg/L and 28.35 µg/L, while the latter ranged between 13.75 µg/L and 19.75 28.35 µg/L (Figure 3-24) over the 2000 to 2015 period. There was an apparent declining trend in DRP concentrations in groundwater from bore E44/0036 (R^2=0.6345). There was no statistically significant difference in DRP concentrations from bore E44/0008 (R^2=0.28) (Figure 3-26).

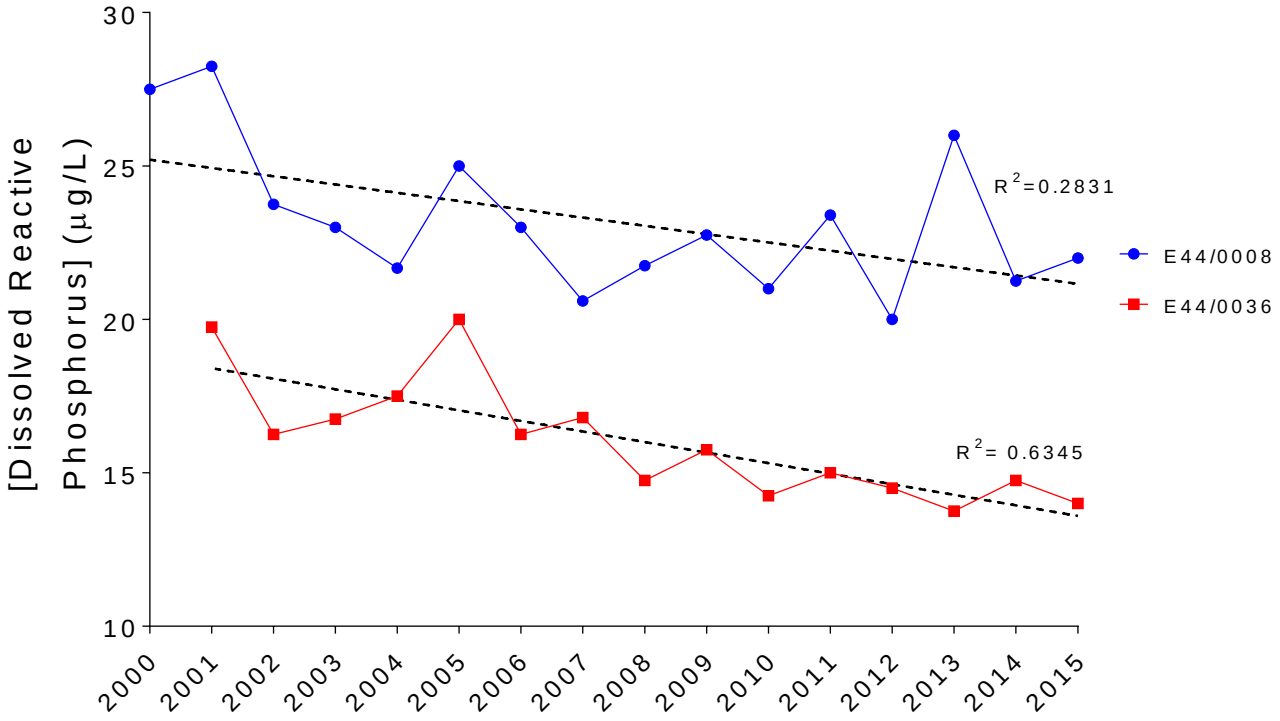

Figure 3-24 Temporal trends in groundwater dissolved reactive phosphorus on the Waimea plains. E44/008 and E44/0036 were monitored for dissolved reactive phosphorus concentrations annually by Environment Southland. Both wells lie within the Balfour nitrate hotspot (for map see Figure 3-18). Annual dissolved reactive phosphorus concentrations between 2000 and 2015 for each bore are displayed.

3.4.2. Surface water nutrients

Nitrate

During 2013, nitrate concentrations increased significantly from the headwaters, i.e. at the largely hill-fed site W-1 (median nitrate concentration 0.5 mg/L) to W-3 (median nitrate concentration 1.4 mg/L), and again to W-5 (median nitrate concentration 4.4 mg/L) (Figure 3-25 a, p-value < 0.05). Nitrate concentrations peaked at W-5, and were then significantly lower downstream at W-7 and W-8 when compared to W-5 (Figure 3-25a, p-value < 0.05). These same trends in nitrate concentration were also significant for the whole 2006-2014 period (Figure 3-25b, p-value < 0.05). During 2013, and over the long term, Longridge stream (L-4) had significantly higher nitrate concentrations than both the lower Waimea (W-8) as well as the other tributaries, Sandstone (S-1) and North Peak Stream (N-1) (Figure 3-25a, p-value < 0.05).

Dissolved reactive phosphorus

In 2013, DRP concentrations increased significantly down the Waimea Stream, from a median of 6.0 µg/L at W-1, to 18.5 µg/L at W-7 (Figure 3-25c, p-value < 0.05). Longridge and Sandstone Streams each had significantly higher median DRP concentrations than the Waimea Stream, with median concentrations of 29.5 µg/L and 40 µg/L respectively (Figure 3-25c, p-value < 0.05). These relationships were also significant for DRP for data collected over the long term (2006-2014) (Figure 3-25d, p-value < 0.05).

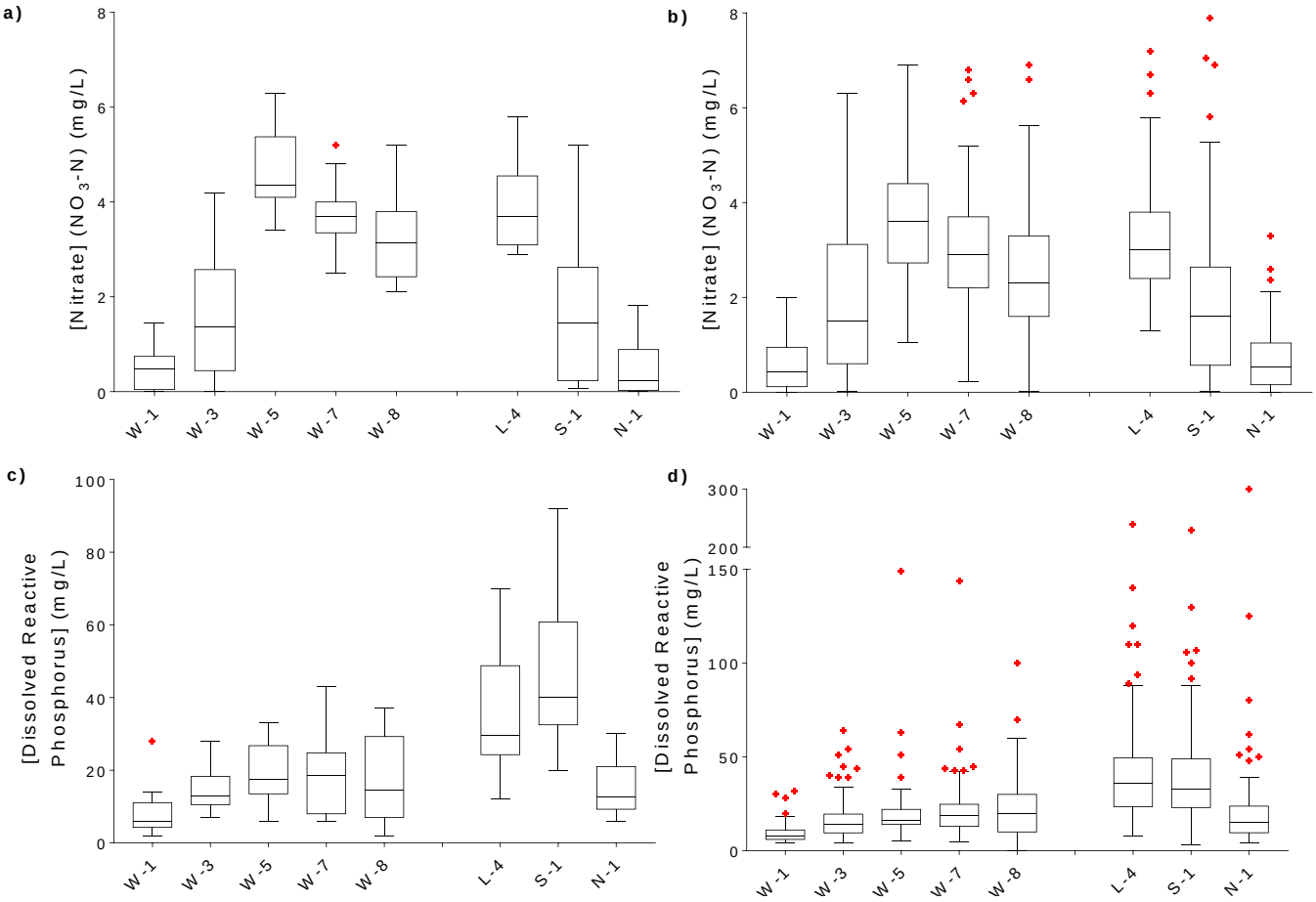

Figure 3-25 Nutrient concentrations in the Waimea Catchment. Nutrient concentrations were monitored by Environment Southland from 2006-2014 at different sites along the Waimea Stream (W-1,3,5,7,8), Longridge Stream (L-4), North Peak Stream (N-1) and Sandstone Stream (S-1) (for locations see Figure 3-1) and the concentration of nitrate (NO_3-N) and dissolved reactive phosphorus was determined. Long term (2006-2014) nutrient concentrations (b,d) are displayed along with nutrient concentrations from 2013 (a,c). Tukey plots with the median and interquartile range are displayed. The whiskers represent 1.5 X interquartile range. Outliers are marked by red crosses.

3.4.3. Annual dynamics of surface water nitrate

Monthly recorded nitrate concentrations for 2006, 2007, 2008 and 2013 were analysed to investigate how the annual nitrate dynamics have varied between 2006 and 2013 (Figure 3-26).

Nitrate concentrations peaked over the winter months, with 2007, 2008 and 2013 all showing a distinctive winter spike in nitrate concentrations. The extent of this winter peak has varied from year to year. In 2006 nitrate concentrations remained below 3 mg/L throughout the year. In 2007 and 2008, nitrate concentrations remained under 3 mg/L over the summer months (November to April), and peaked over the winter months to concentrations greater than 5 mg/L (Figure 3-26).

In, 2013 nitrate concentrations in the Waimea Stream peaked over the winter months in the upper part of the catchment at W-1 and W-3, rising to approximately 4-5 mg/L, from summer concentrations of below 1.0 mg/L. In the lower Waimea catchment however, at W-5, W-7 and W-8, nitrate concentrations, while peaking over the winter months, also remained elevated (> 3.0 mg/L) over summer. Longridge stream (L-4) too exhibited elevated nitrate during summer (> 2.0 mg/L). Sandstone however did not have elevated summer nitrate, with nitrate concentrations dropping to 1.0 mg/L and below over the summer months during 2013 (Figure 3-25d).

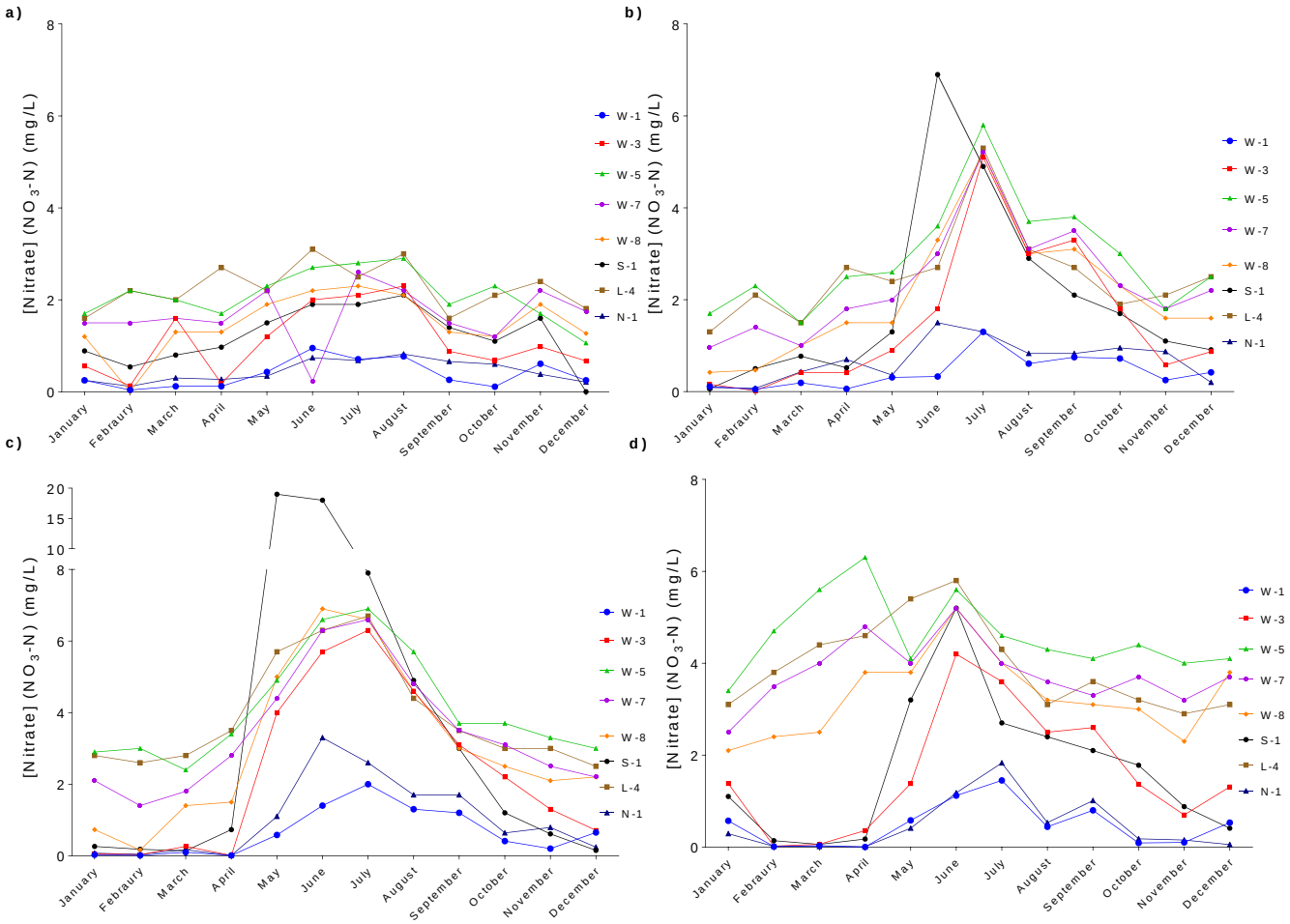

Figure 3-26 Annual trends in nitrate (NO_3-N) on the Waimea Stream. Nutrient concentrations were monitored by Environment Southland from 2006-2014 at different sites along the Waimea Stream (W-1,3,5,7,8), Longridge Stream (L-4), North Peak Stream (N-1) and Sandstone Stream (S-1) (for locations see Figure 3-1) and the concentration of nitrate (NO_3-N) was determined. Here monthly nitrate concentrations are displayed for a) 2006, b) 2007, c) 2008 and d) 2013.

3.4.4. Mean summer and winter surface water nitrate concentrations between 2006 and 2013.

Summer nitrate concentrations have remained unchanged in the upper half of the Waimea Stream at W-1 and W-3, while having slowly increased in the lower half of the Waimea Stream, between 2006 and 2013 (Figure 3-27). In the summer of 2006 there were mean nitrate concentrations of 0.14 mg/L and 0.76 mg/L recorded for the Waimea Stream at W-1 and W-3 respectively. In 2013, the mean summer concentrations were recorded as 0.20 mg/L and 0.48 mg/L respectively, with no statistically significant difference compared to 2006 ($p > 0.05$). The Waimea Stream at W-5, W-7 and W-8 had mean nitrate summer concentrations during 2006 of 1.97 mg/L, 1.53 mg/L and 0.83 mg/L respectively. In 2013, these had increased to 4.57 mg/L, 3.33 mg/L and 2.20 mg/L respectively. At W-5, W-7 and W-8 there has been a statistically significant increase in summer nitrate concentrations. A linear regression analysis reveals a positive significant trend in increasing nitrate for these three sites, with r^2 values of 0.89, 0.9 and 0.69 for W-5, W-7 and W-8 respectively. On average, summer nitrate concentrations have increased by 0.33 mg/L, 0.23 mg/L, and 0.17 mg/L per year at W-5, W-7 and W-8 respectively. Between 2006 and 2013 there was no significant increase or decrease in nitrate concentrations across all sites on the Waimea Stream (Figure 3-27b).

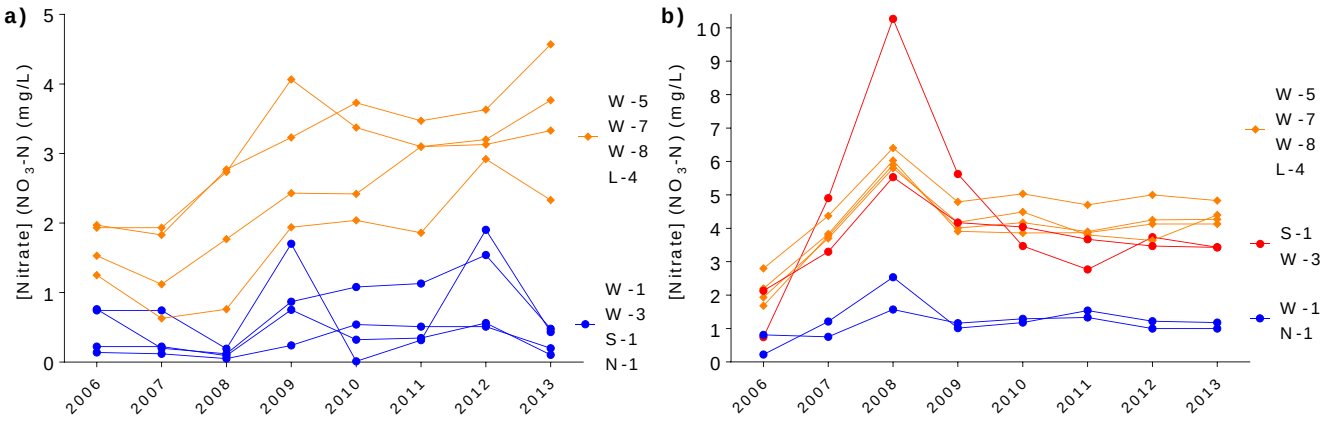

Figure 3-27 Summer and winter nitrate concentrations in the upper and lower Waimea Stream. Nutrient concentrations were monitored by Environment Southland from 2006-2014 at different sites along the Waimea Stream (W-1,3,5,7,8), Longridge Stream (L-4), North Peak Stream (N-1) and Sandstone Stream (S-1) (for locations see Figure 3-1) and the concentration of nitrate (NO_3-N) was determined. The mean nitrate (NO_3-N) concentration for a) January to March (summer) and b) July to August (winter) between 2006 and 2013 is displayed.

When the differences between summer (January-March) and winter (June-August) nitrate concentrations were compared between period 2006-2008 and 2001-2013, there has been no significant change in winter nitrate concentration in either the upper (W-1,W-3) or lower (W-5,7,8) Waimea Stream (Figure 3-28). There has been no significant change in summer nitrate concentrations in the upper Waimea Stream (W-1 and W-3) (Figure 3-28). However, there has been a significant increase in summer nitrate concentrations in the lower Waimea Stream, from a median concentration of 1.5 mg/L during 2006-2008, to a median of 3.1 mg/L during 2011-2013 (Figure 3-28).

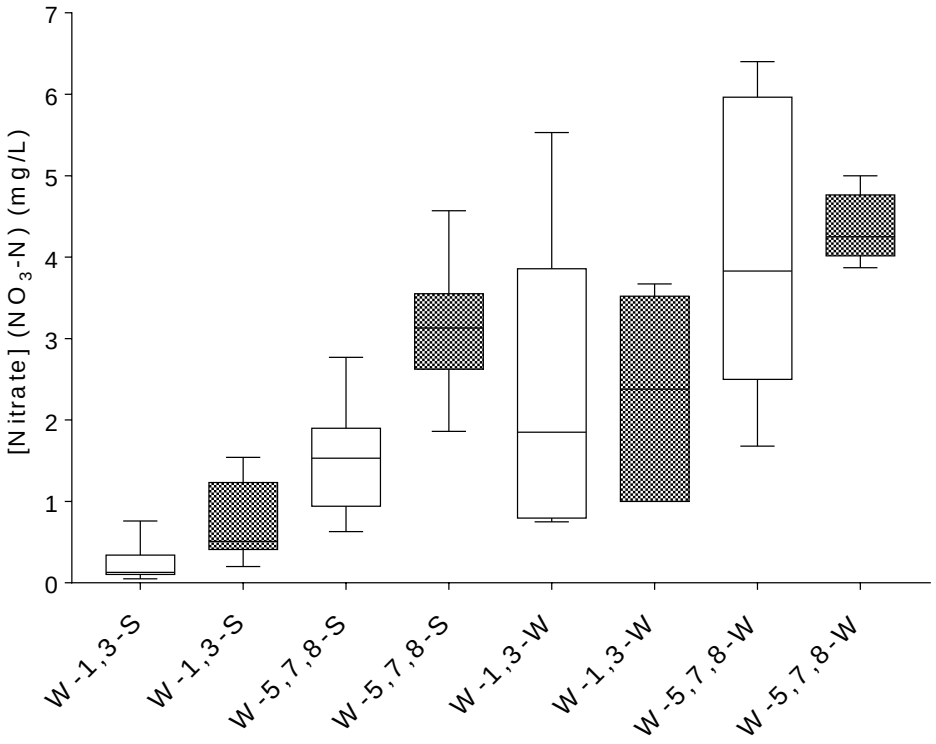

Figure 3-28 Nitrate concentrations during summer and winter in the Waimea Catchment. Nitrate concentrations were monitored by Environment Southland from 2006-2014 at different sites along the Waimea Stream (W-1,3,5,7,8) (for locations see Figure 3-1). Here nitrate concentrations from 2006-2008 (clear boxes) are compared to nitrate concentration from 2011-2013 (shaded boxes) for the upper Waimea Stream (W-1 and W-3) and the lower Waimes (W-5,7,8) between summer (S) and winter (W). Summer values include data collected during January to March, winter values include data collected during June to August.

3.4.5. Flow and surface water nitrate

There was a significant positive correlation between flow and elevated nitrate concentrations at W-1, W-3, N-1 and S-1 (r^2 between 0.59 & 0.61) (Figure 3-29). This was a non-linear relationship, with elevated nitrate reaching a saturation point once a certain flow had been reached. Plots where the flow data has been log transformed are also displayed to illustrate the relationship. At W-5,7,8, S-1 and L-4 there was no significant correlation between flow and nitrate concentration (Figure 3-29).

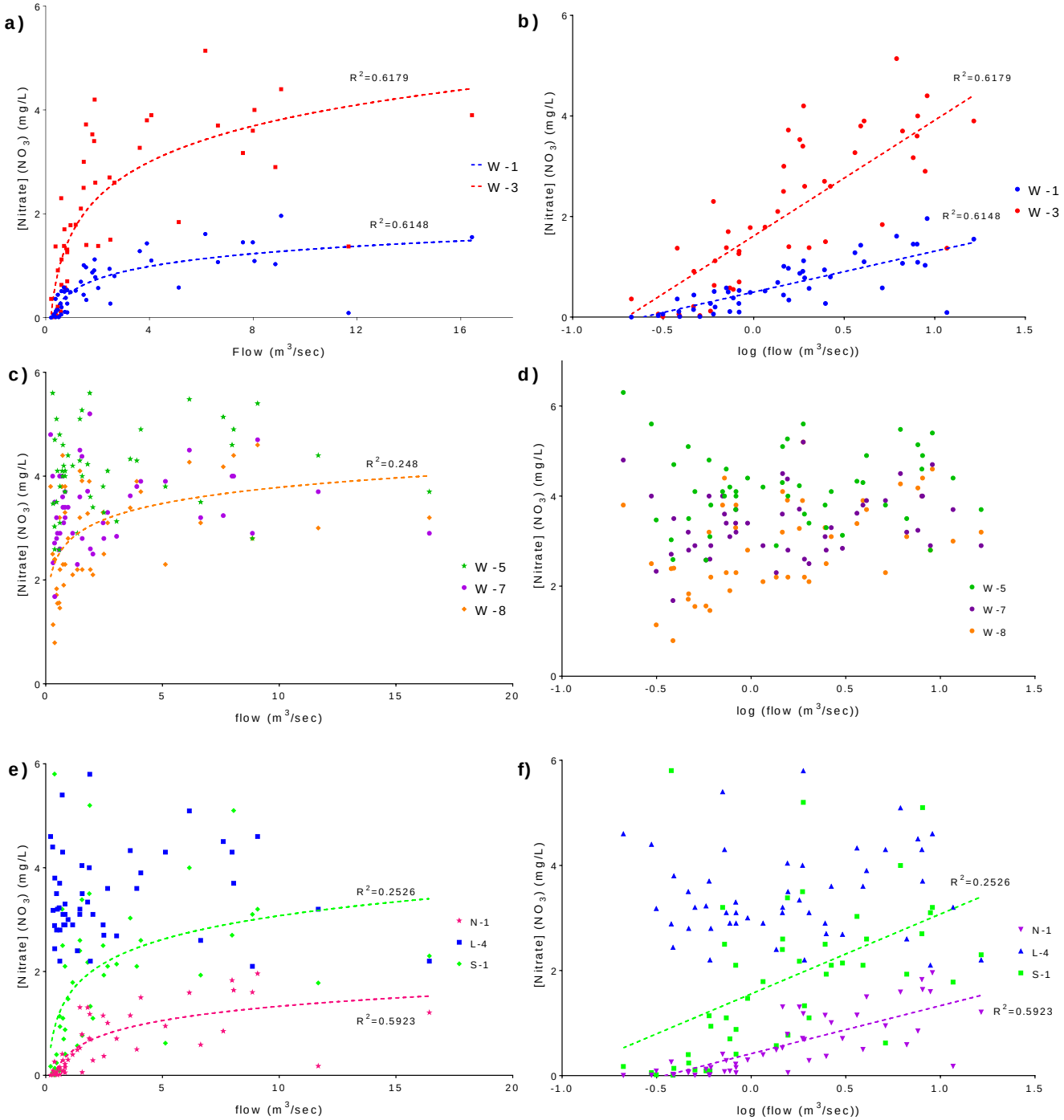

Figure 3-29 Nitrate concentrations and in-stream flow. Nitrate concentrations were monitored by Environment Southland from 2006-2014 at different sites along the Waimea Stream (W-1,3,5,7,8) Longridge Stream (L-4), North Peak Stream (N-1) and Sandstone Stream (S-1) (for locations see Figure 3-1). Nitrate concentrations have been plotted against flow (a,c,e) and log transformed flow (b,d,e). Flow data is the mean flow of the Waimea Stream at Mandeville on the day data was collected. Nitrate is plotted against flow for a,b) the upper Waimea Stream (W-1 and W-3), c,d) the lower Waimea Stream (W-5,7,8), and e,f) the Waimea Stream tributaries N-1,L-4 and S-1.

3.5. Hydrochemistry and nitrate

3.5.1. Surface water ions and nitrate

Surface water nitrate was related to surface water hydrochemistry in order to make connections between different end-member hydrochemical signatures and elevated in-stream nitrate. Elevated SO_4 was used as a signature of lateral flow through the soil zone, principally during wet periods of high flow, while elevated Na was used as a signature of groundwater dominating dry periods of low flow.

Concentrations of SO_4 correlated strongly with elevated nitrate concentrations at W-1, W-3, N-1 and S-1, whereas at W-5, W-7, W-8 and L-4 there was no correlation (Figure 3-30a,b). As Na concentrations increased in surface water at W-1, N-1 and S-1, there was a corresponding decline in nitrate. This relationship was less apparent at W-3, although elevated Na concentrations corresponded to lower nitrate concentrations. In the lower Waimea Stream (W-5,7,8) and Longridge stream, elevated Na concentrations did not correspond to any decline in nitrate concentrations (Figure 3-30c).

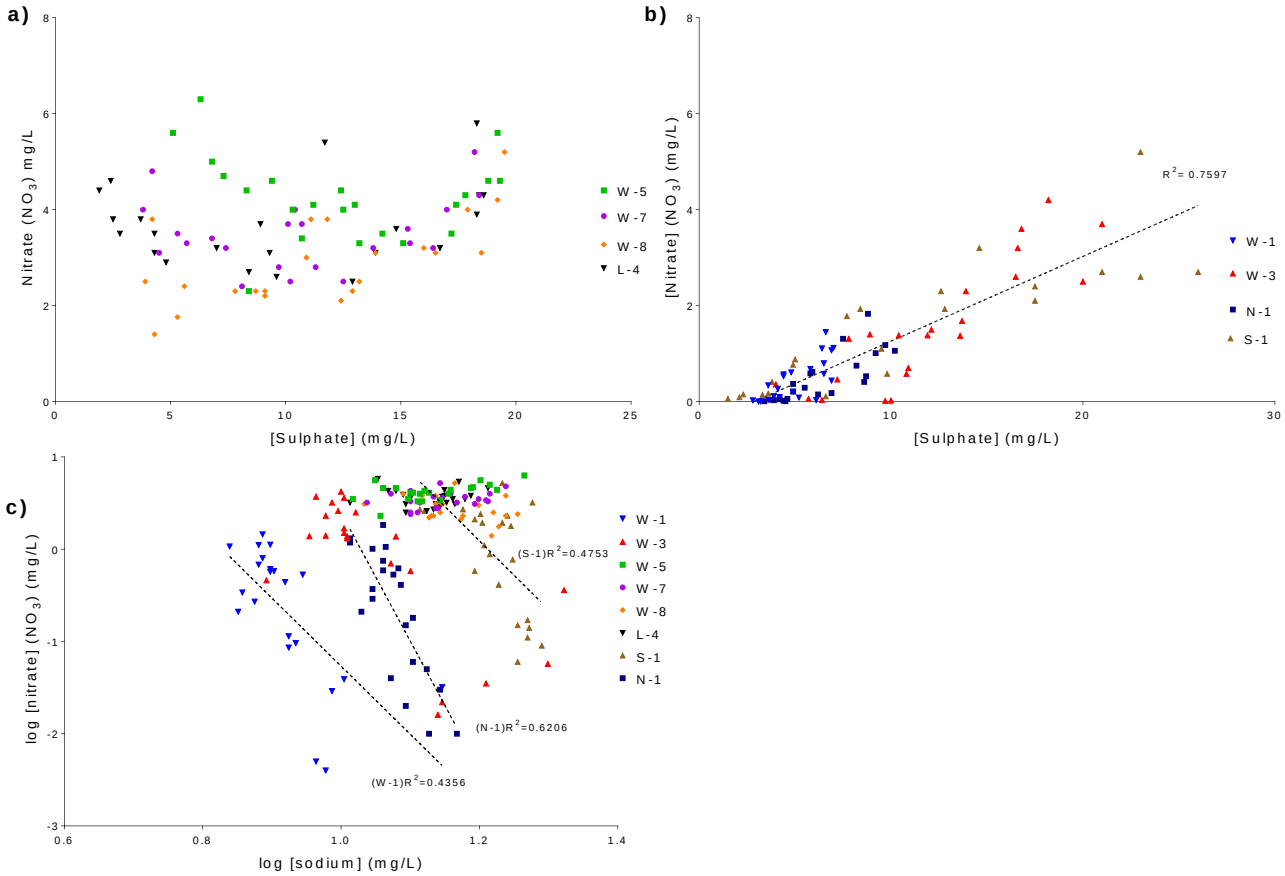

Figure 3-30 Relationship between surface water chemistry and nitrate concentrations. Nitrate, sulphate and sodium concentrations were monitored by Environment Southland for 22 months from September 2012 to June 2014. Here nitrate concentrations are plotted against sulphate for a) W-5, W-7, W-8 and L-4, and for b) W-1, W-3, N-1 and S-1, (the linear regression includes all sites plotted) and against c) log concentration of sodium for all sites (linear regressions for W-1, N-1 and S-1 displayed.

3.5.2. Groundwater major ions and nitrate

In this section groundwater nitrate concentrations were compared to a suite of major ions. There was a strong correlation between elevated Na, Ca, Mg and elevated nitrate concentrations from groundwater within the 'Balfour nitrate hotspot' (Figure 3-31) (R^2 value of 0.74, 0.82 and 0.71 respectively). This correlation was less strong between nitrate and K was but still apparent with an R^2 value of 0.43. There was no apparent relationship between HCO_3 and nitrate or between SO_4 and nitrate concentrations in groundwater.

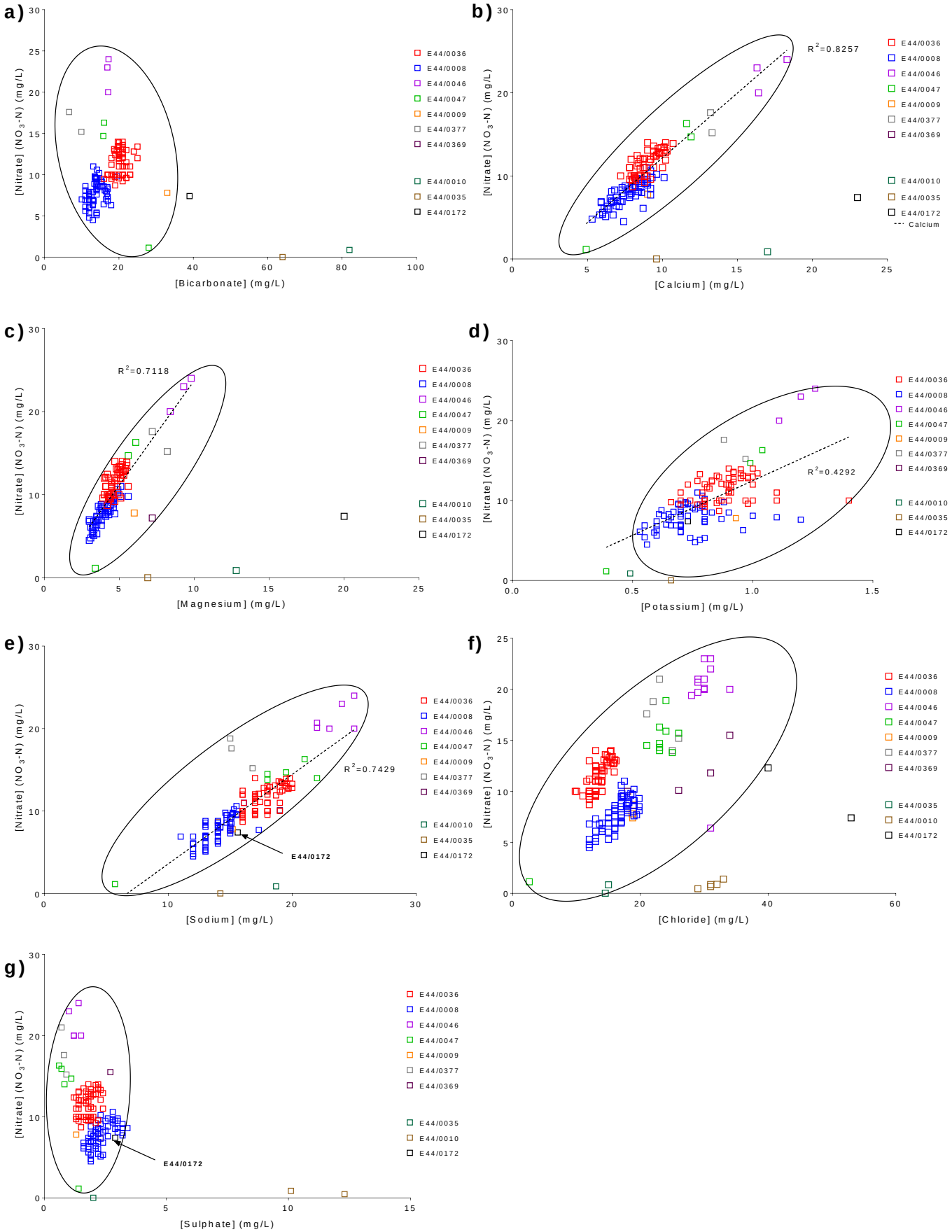

Figure 3-31 Nitrate and major ions in groundwater on the Waimea Plains. The water chemistry and nitrate concentration of groundwater has been monitored by Environment Southland for various bores across the Waimea Plains between 2001 and 2015 (for locations see Figure 3-18). E44/0036, E44/0035 and E44/0172 lie outside of the Balfour nitrate hotspot. The remaining bores all lies within the Balfour nitrate hot spot. Linear regressions include data from bores within the nitrate hotspot which has been circled on each plot. In e) and g) E44/0172 lies within this circle and has been highlighted.

3.1. Summary

3.1.1. Surface water hydrochemistry

Spatial variation in hydrochemistry

- The concentration of Cl, Na, K, SO_4, Ca and HCO_3 all increased significantly between the headwaters (W-1) and middle reaches (W-4,5) of the Waimea Stream.
- Si and Mg were significantly elevated in the mid Waimea Stream (W-5) compared to both upstream and downstream sites on the Waimea Stream.

Seasonal variation in hydrochemistry

Summer surface water was characterised by:

- Elevated Na and HCO_3
- Elevated Na:Cl ratio
- Low SO_4, K and Ca

Winter surface water was characterised by:

- Elevated SO_4, K and Ca
- A Na:Cl ratio similar to marine aerosols
- Low Na and HCO_3

3.1.2. Groundwater chemistry

HCO_3, Cl, and Na dominated the chemistry of the Waimea plains groundwater. The groundwater can be characterised as HCO_3 and Cl type waters, with the later occurring principally within the Balfour nitrate hotspot and in the lower half of the Waimea Plains, while the former occurred in the upper Waimea Plains.

Groundwater across the Waimea Plains had a significantly elevated Na:Cl ratio relative to that of marine aerosols, while the SO_4:Cl ratio of groundwater was below that of marine aerosols.

A number of major ions exhibited a gradual yet significant increase over the period 2000 to 2015. Seasonally, the chemistry of the groundwater did not appear to alter significantly.

Nitrate concentrations within the Balfour nitrate hotspot have shown a strong increasing trend in nitrate concentrations (>11.3 mg/L), while outside of the nitrate hotspot, nitrate concentrations have remained relatively low (<2.0 mg/L). DRP concentrations from bore E44/0036 showed a gradual declining trend, between 2000 and 2015.

3.1.3. Surface water nutrients

Surface water DRP concentrations increased in the Waimea Stream significantly from the headwaters and mid Waimea Stream. DRP concentrations in both Longridge and Sandstone Stream were significantly higher than in the lower Waimea Stream.

Nitrate concentrations increased significantly from the upper to mid Waimea Stream. They were also elevated over winter throughout the Waimea catchment, however, in the mid to lower Waimea Stream, and lower Longridge Stream, they were also elevated over summer as well. Average summer nitrate concentrations have gradually increased in the mid to lower Waimea Stream between 2006 and 2013, while remaining unchanged in the upper Waimea Stream over this period.

3.1.4. Key findings to be tested during 2016 monitoring

For the purpose of establishing groundwater inputs of nitrate to the Waimea Stream, the following key findings were further tested in chapter 4 through data collection and analysis carried out by the author in 2016.

Hydrochemistry

The chemical character of summer low flows and winter high flows have been identified.

High flow during wet periods was characterised by:

- Elevated SO_4 and a high SO_4:Cl ratio.
- Elevated Ca and K.
- Low HCO_3 and Na concentrations.
- Low Na:Cl ratio (approximating the marine aerosol ratio of 0.55).

Low flow during dry periods was characterised by:

- Elevated Na and HCO_3 concentrations.
- Low SO_4 concentrations and a low SO_4:Cl ratio.
- Low Ca and K concentrations.
- Elevated Na:Cl ratio (median of 0.94).

Nutrients

DRP was found to increase significantly between the upper and lower Waimea Stream. DRP was also found to be significantly higher in Longridge and Sandstone Stream compared to the Waimea Stream.

Two key finding regarding nitrates may shed light on whether groundwater derived nitrate is contributing to in-stream nitrate.

- Nitrate concentrations increased substantially in the middle reaches of the Waimea Stream (between W-3 and W-5).
- Nitrate concentrations in the upper Waimea Stream were elevated only over winter, while in the lower Waimea Stream nitrate concentration remained elevated during both winter and summer.

Chapter 4 Results: Analysis of Waimea Catchment Monitoring 2016

The following chapter presents data collected by the author from the Waimea catchment during 2016 (February and July) was analysed. Data was obtained monthly from eight sites along the Waimea Stream (W-1 to W-8), and four sites on Longridge Stream (L-1 to L-4) (for map see Figure 2-1). The data spans the mid to late summer period through to mid-winter. The purpose of this study was to test the findings reached in Chapter 3, as well as explore further avenues that may shed light on the nutrient flow paths and surface-groundwater interactions of the Waimea Stream catchment.

Firstly, the climatic conditions of the study period were surveyed. This was done in order to relate the hydrological conditions at the time of sampling to in-stream hydrochemistry. Water quality and hydrochemistry was then canvassed spatially between different reaches, and temporal shifts between summer and winter were investigated. This was done in order to establish the chemistry of low base flow conditions and high flow conditions. Sediment chemistry was then investigated for both the Longridge and Waimea Streams. Finally, the stable isotopes of hydrogen, oxygen and carbon were utilised to further investigate and establish the connectivity between the groundwater of the Waimea Plains and the Waimea Stream.

4.1. Climatic conditions during 2016 monitoring period

In this section, the climatic conditions during the study period are presented along with the flow levels on the day of sampling for each month. Rainfall and Penman potential evapotranspiration data was obtained from NIWA, from a monitoring station at Riverdale, York Road (station number: 38645. Latitude: -45.904, longitude: 168.739) (NIWA, 2016), while average monthly rainfall for Balfour, along with the flow of the Waimea Stream at Mandeville (W-8), has been obtained from Environment Southland (Environment Southland, 2016). Flow gauging was undertaken at each site from February through to July. However, during July the flow levels in the Waimea and Longridge Streams were too high to safely gauge at all sites. Flow data obtained for July is displayed where it is available.

Monthly rainfall, evapotranspiration and in-stream flow

Average monthly rainfall on the Waimea Plains does not vary greatly seasonally (Figure 4-1). Between February and July accumulated averages fluctuate approximately between 60 mm and 80 mm per month. In 2016, February, May and June had relatively high rainfall (100-120 mm), while March, April and June all had accumulated monthly rainfalls of approximately 20-40 mm. There was, however, a significant seasonal change in the level of evapotranspiration that occurred, which during February exceeded average rainfall for that month at close to 100 mm, while in May, June and July it was less than 20 mm a month (Figure 4-1d). Thus in the winter months, wetter conditions and higher flows were largely a result of lower levels of evapotranspiration, rather than higher rainfall.

Recorded in-stream flows during each month largely reflected this dynamic of rainfall relative to the level of evapotranspiration occurring (Figure 4-1). Thus, although February and July received similar amounts of rainfall, the Waimea Stream at Mandeville (W-8) during July had in-stream flows several orders of magnitude greater than that during February (280 L/sec Vs. 22000 L/sec) (Figure 4-1b). February to April all recorded approximately similar flow levels. May had higher flow levels than June which was reflected in the low levels of rainfall during June. Flow levels in Longridge Stream largely mirrored the relative monthly flows in the Waimea Stream (Figure 4-1c).

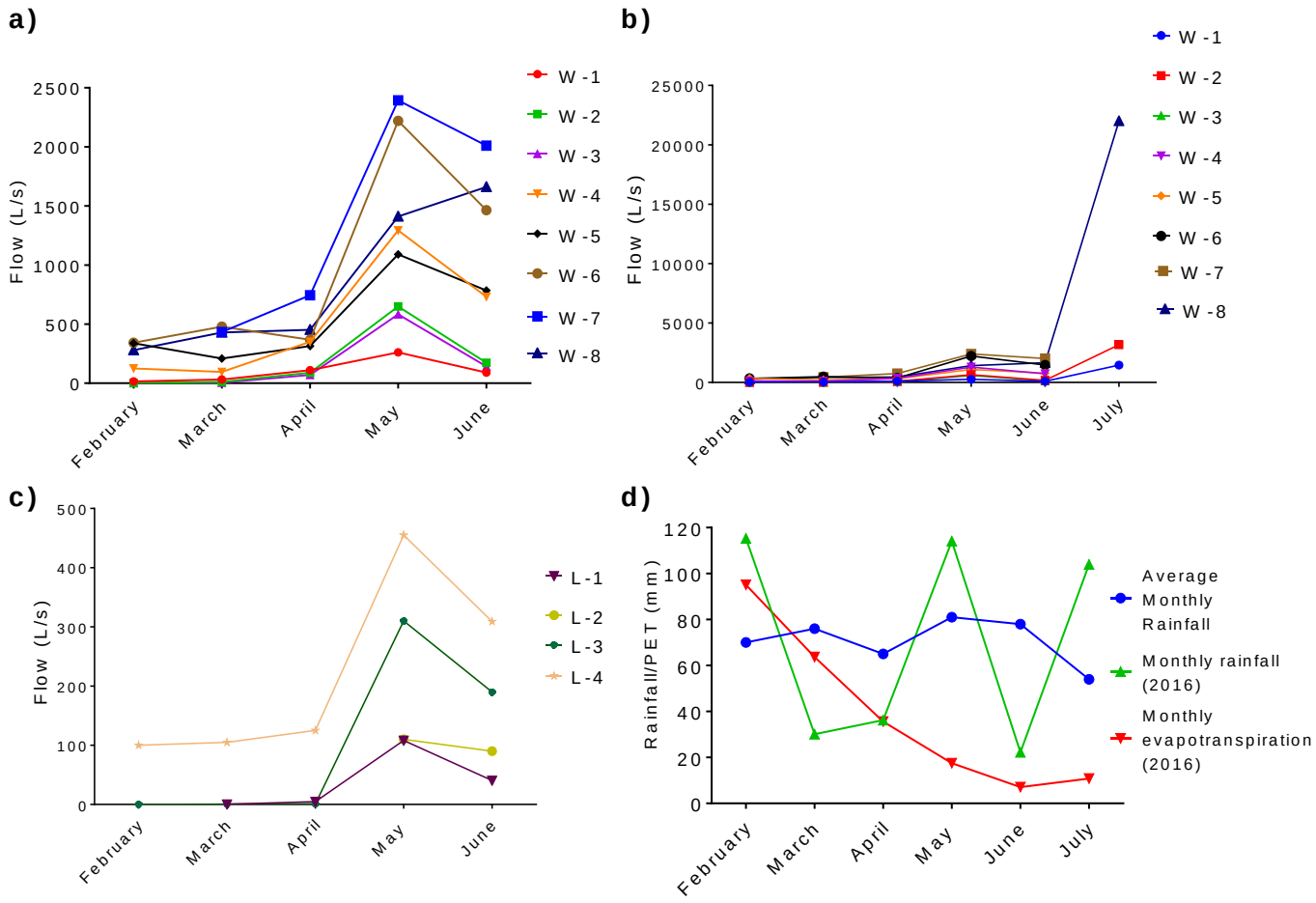

Figure 4-1 Monthly flow, rainfall and evapotranspiration of the Waimea and Longridge Streams. Flow gauging was undertaken at each site on the day of sampling on the Waimea Stream (a,b) and Longridge Stream (c) (for map see Figure 2-1). Flow data for the Waimea Stream at Mandeville (W-8) has been obtained from Environment Southland (Environment Southland, 2016). Monthly accumulated rainfall and Penman evapotranspiration (d) data has been obtained from NIWA (Riverdale, York Road (station number: 38645. Latitude: -45.904, longitude: 168.739) (NIWA, 2016), while long term average monthly rainfall has been obtained from Environment Southland (Environment Southland, 2016).

In-stream flow at each site

During March and April, flow in the upper Waimea stream was relatively stable from W-1 through to W-3, before increasing substantially between W-3 and W-4 (Figure 4-1a). This is approximately the stretch of river where previous concurrent flow gauging has indicated a substantial gain in flow (K. Wilson, 2010). During May, which saw higher levels of rainfall than June, this dynamic shifted slightly, with more flow gains apparent between W-1 and W-3, which may reflect a greater level of overland flow contributing to flow in the upper Waimea catchment during the May monitoring period. In July, flow levels in both the Waimea and Longridge Streams were of at least an order of magnitude greater than that of the previous five months (Figure 4-2c,d).

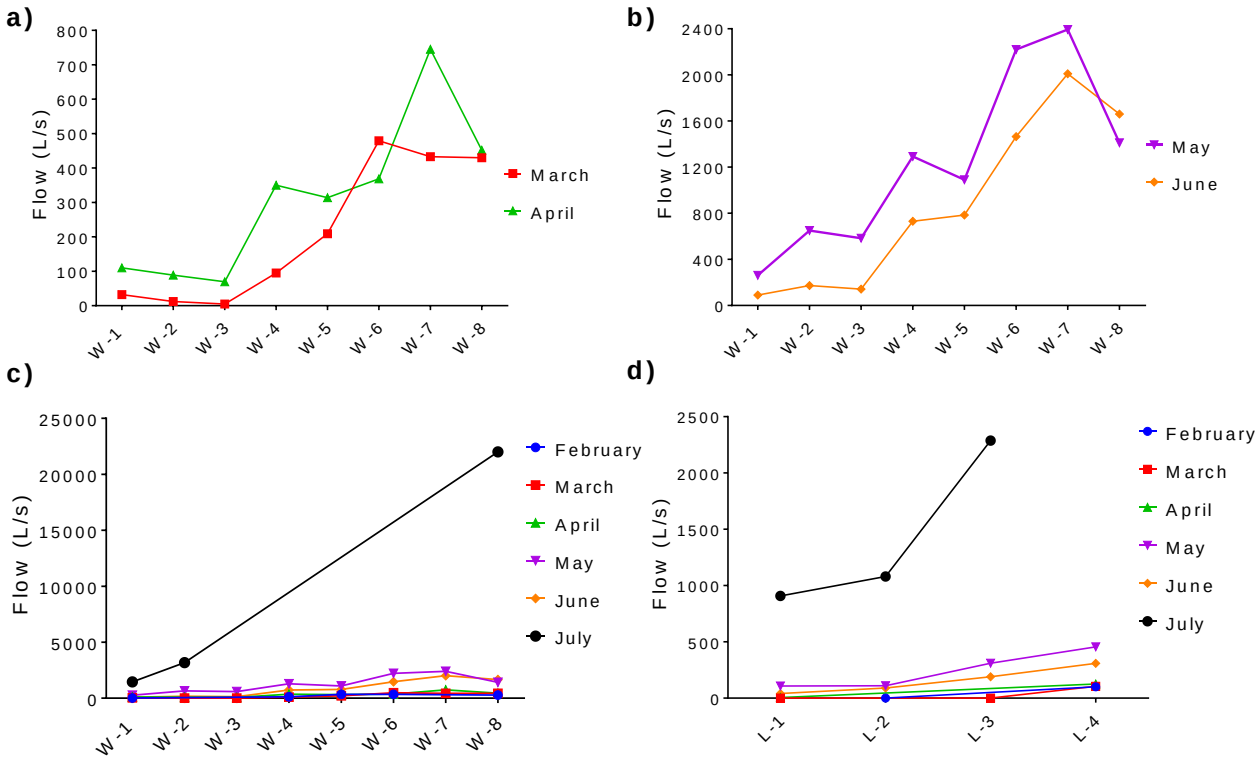

Figure 4-2 Flow of Waimea and Longridge Stream at each site. Flow gauging was undertaken at each site on the day of sampling for the Waimea Stream (W-1 to W-8) and Longridge Stream (L-1 to L-4) (for map see Figure 2-1). Flow data for the Waimea Stream at Mandeville has been obtained from Environment Southland (Environment Southland, 2016). Here flow in the Waimea Stream (W-1 to W-8) is displayed for a) March and April, b) May and June c) February to July, and for d) Longridge Stream from February to July.

4.2. Surface water chemistry

Spatial and temporal variation in surface water chemistry is analysed in this section (raw data see appendix A and B).

4.2.1. Basic water quality

The median pH at all sites ranged between 6.9 and 7.5. The pH at W-2, L-1 and L-2 was significantly lower than at the lower Waimea at W-6 (p-value < 0.05). The median temperature at all sites ranged between 9.2˚ C at W-2 to 12.6˚ C at L-3. Median temperatures were relatively comparable across the Waimea and Longridge Streams, with no statistically significant differences found between the sites (Figure 4-3). Median dissolved oxygen concentrations at all sites were between 10 and 12 mg/L. The headwaters of Longridge Stream (L-1 and L-2) had markedly lower minimum dissolved oxygen concentration of approximately 2.2 mg/L (Figure 4-3).

Conductivity increased significantly, from a median of 95 µs/cm at W-1 to 213 µs/cm at W-4 (p-value < 0.05). Conductivity in the lower Longridge Stream at L-3 and L-4 was comparable to the mid to lower Waimea Stream (W-4 to W-8) with median conductivities of approximately 180-200 µs/cm. Conductivity at L-2 on Longridge stream had significantly higher conductivity levels than L-1, the other head water site of the Longridge Stream (p-value < 0.05) (Figure 4-1c). Turbidity was significantly higher on the Waimea Stream at W-8, with a median of 8.5 FAU, compared to a median of 3.5 at the headwater site at W-1, which had a median of 3.5 FAU (Figure 4-3c). The headwaters of Longridge Stream had the highest turbidity of all sites, recording a median of 13.5 FAU.

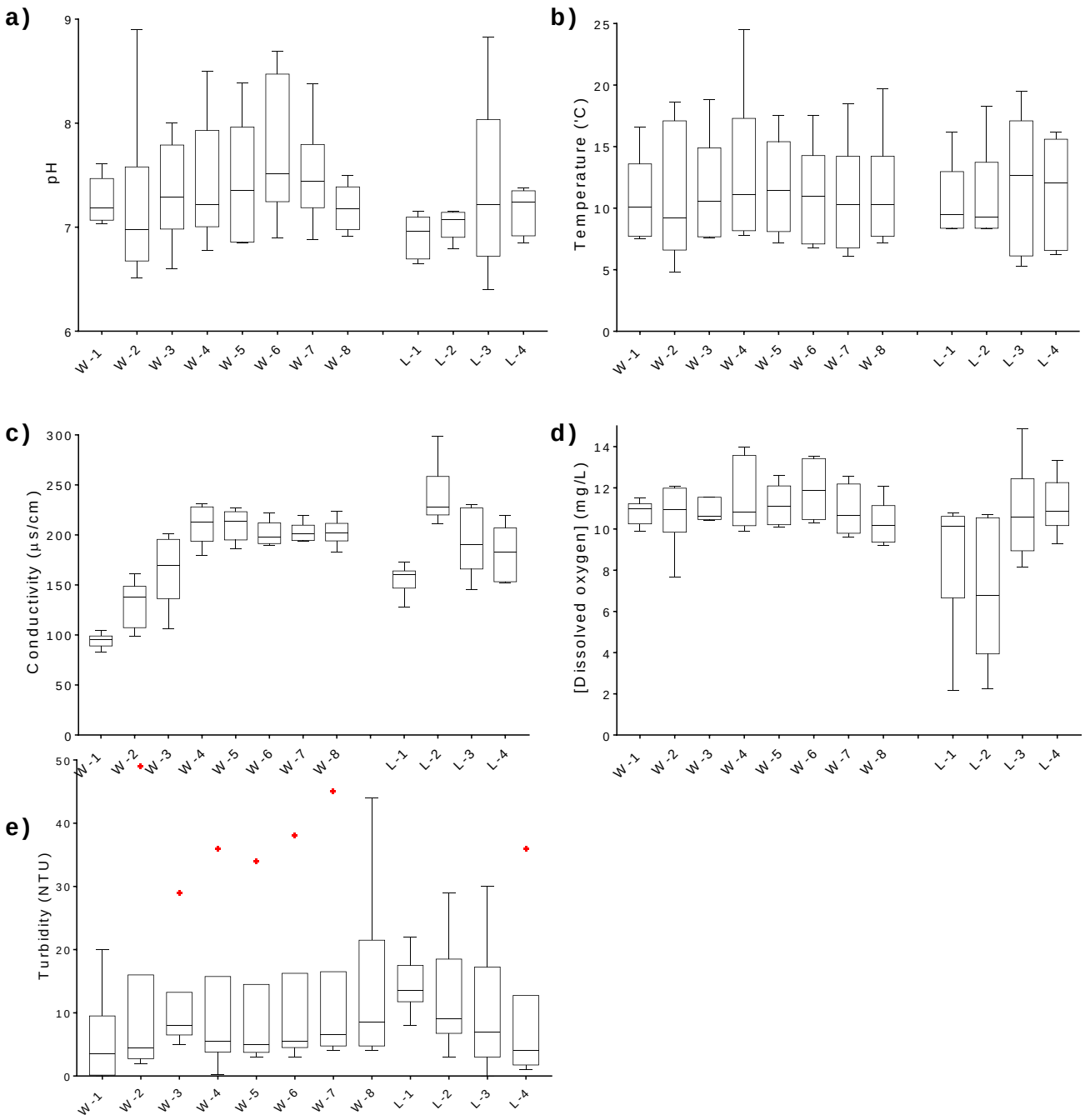

Figure 4-3 Basic water chemistry of Waimea and Longridge Streams. Water quality was monitored monthly for six months for different sites along the Waimea and Longridge Streams (W-1-8 and L1-L-4) (for map see Figure 2-1), respectively, and the **a)** pH, **b)** Temperature, **c)** conductivity **d)** dissolved oxygen and e) turbidity were determined. Tukey plots with median and interquartile range from six measurements are shown.

4.2.2. Spatial variation in chemistry

In this section spatial variation in major ion chemistry as well as the trace metals and metalloids; Fe, Mn, Al and B were investigated for the Waimea (W-1-8) and Longridge Streams (L-1-4).

Major ions

The concentration of all major ions in the Waimea Stream mirrored the downstream increase in conductivity between the hill-fed site at W-1 through to W-4 (Figure 4-4). Cl, Mg, Ca and SO_4 all increased significantly between W-1 and W-4 (p-value < 0.05). Na increased steadily from W-1 right through to W-5

(p-value < 0.05). K increased significantly between W-1 and W-2 (p-value < 0.05). HCO_3 concentrations at W-4 and W-5 were significantly higher than at W-1, rising from a median of 33.1 mg/L to approximately 50.0 mg/L at W-4 and W-5 (Figure 4-4). Mg was significantly higher in the Waimea Stream at W-4, when compared to all other sites on the Waimea Stream except for W-5 (p-value < 0.05). From W-4 through to W-8 concentrations all major ions, bar Mg, remained at similar concentrations.

SO_4 and K concentrations in Longridge Stream were similar to those of the mid to lower Waimea Stream, and were only significantly higher than W-1 on the Waimea Stream (p-value < 0.05).

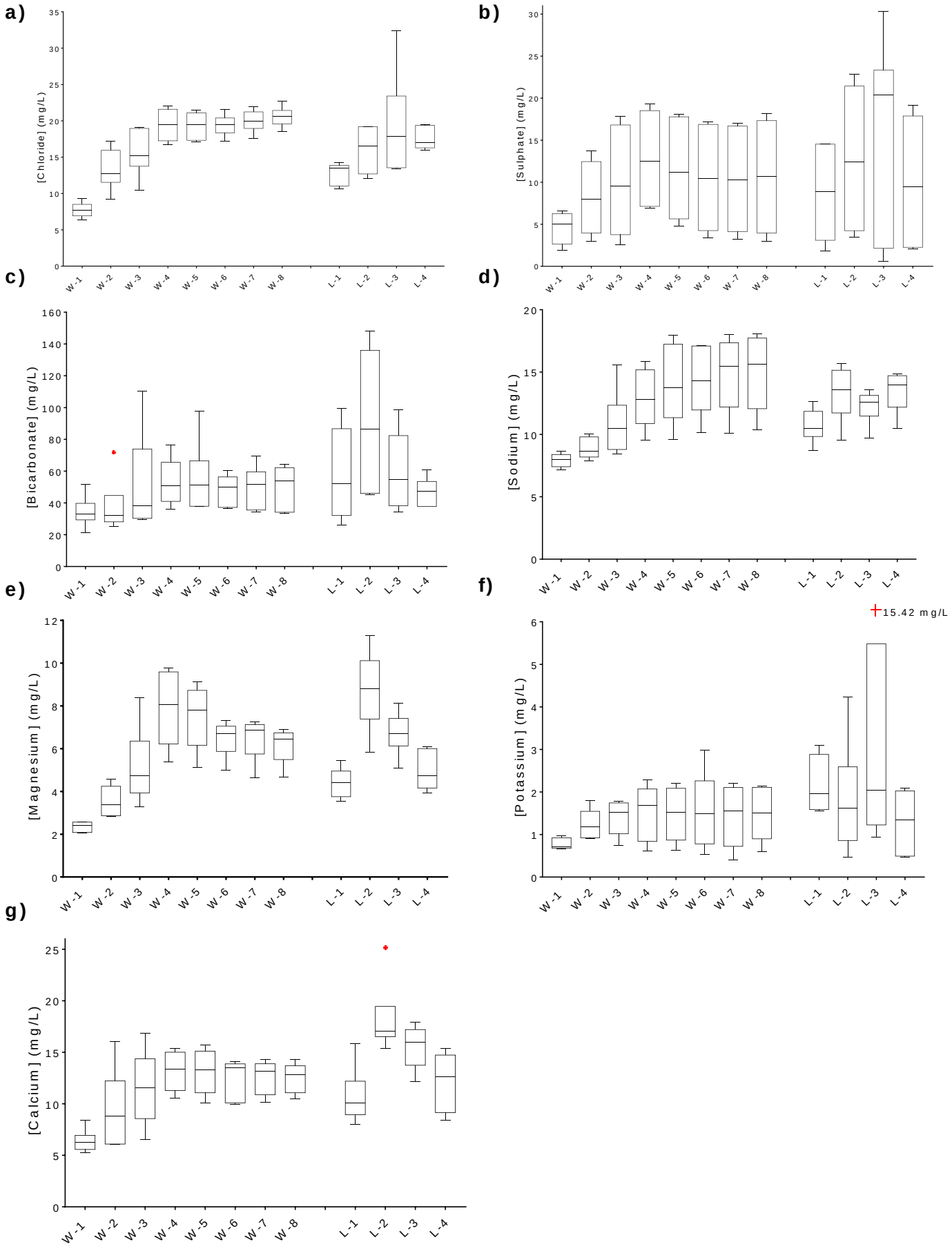

Figure 4-4 Spatial major ion chemistry of the Waimea and Longridge Streams. Water samples were collected monthly from the Waimea Stream (W-1 to W-8) and from Longridge Stream (L-1 to L-4) (for map see Figure 2-1) for six months and were analysed for a) chloride, b) sulphate, c) bicarbonate, d) sodium, e) magnesium, f) potassium and g) calcium. Tukey plots with median and interquartile range from six measurements are shown. Whiskers are 1.5X the interquartile range, red crosses are outliers.

Trace elements

The concentration of dissolved Fe was generally elevated in the headwater sites of both the Longridge and Waimea Streams, while dissolved Mn was elevated in the headwaters of Longridge Stream (Figure 4-5). The concentration of Al did not vary significantly between sites, while boron increased significantly between W-1 and W-3 on the Waimea Stream.

On the Waimea Stream Fe concentrations at W-3 were significantly higher than at W-4 (Figure 4-5a) (p-value < 0.05). At W-3 the median Fe concentration was approximately 200 µg/L, compared to approximately 90 µg/L at W-4. The rest of the Waimea Stream from W-5 to W-8 had Fe concentrations of approximately 100 µg/L. There was no significant difference in Al or Mn concentrations across the sites on the Waimea Stream (Figure 4-5a). Concentrations of B increased significantly between W-1 and W-3 on the Waimea Stream (Figure 4-5c) (p-value < 0.05).

L-1 on Longridge Stream had significantly higher concentrations of Fe than the Waimea Stream at W-4 and W-5, with a median Fe concentration of 650 µg/L. L-1 also had a median Mn concentration of 66 µg/L, which was significantly greater than the Longridge Stream at L-4. All other sites on Longridge Stream recorded median concentrations of Fe and Mn half that of L-1 (Figure 4-3).

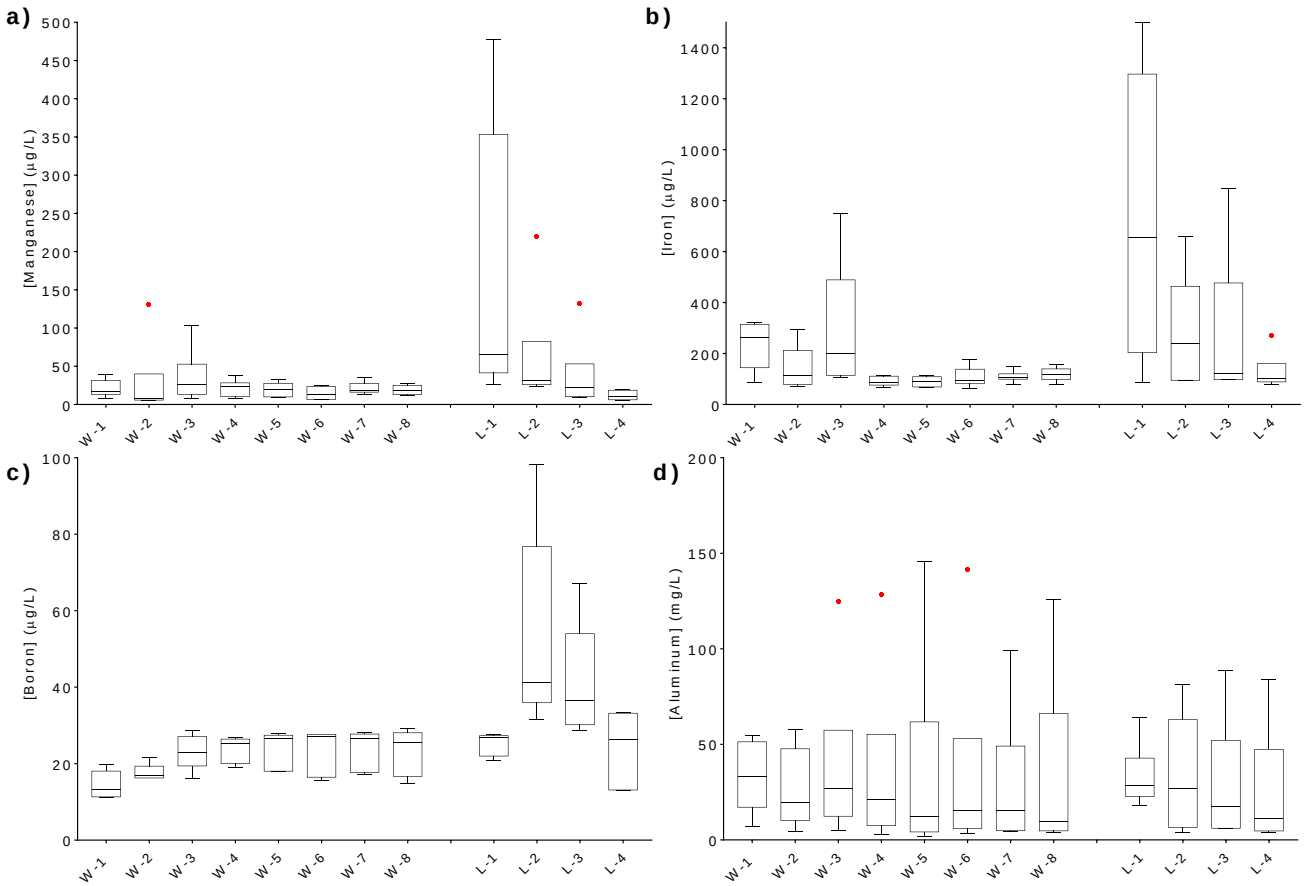

Figure 4-5 Spatial trace element chemistry of the Waimea and Longridge Streams. Water samples were collected monthly from the Waimea Stream (W-1 to W-8) and from Longridge Stream (L-1 to L-4) (for map see Figure 2-1) and were analysed for a) Manganese, b) iron, c) Boron, d) aluminium. Tukey plots with median and interquartile range from six measurements are shown. Whiskers are 1.5X the interquartile range, red crosses are outliers.

4.2.3. Seasonal variation in surface water chemistry

In this section, the mean major ion concentrations of summer and winter have been contrasted in order to establish any significant seasonal shifts in major ion composition (Figure 4-6 & Figure 4-7). Summer major ion proportions are a mean of February and March data, while winter proportions were a mean of June and July data. For this analysis ion proportions have been based on meq/L.

Waimea Stream ion proportions

During summer all sites were dominated by HCO_3 (Figure 4-6). The dominant cation varied across different reaches. The headwater site at W-1 had HCO_3-Na-Ca type waters, with both Na and Ca of equal proportions. W-2 and W-3 had HCO_3-Ca type waters. W-4 had HCO_3-Mg type waters, while W-5 had HCO_3-Mg-Na type waters with Na and Mg of equal proportion. The lower Waimea, from W-6 to W-8, had HCO_3-Na type waters.

There was a shift in major ion composition between summer and winter (Figure 4-6). There was a decrease in HCO_3 across all sites. HCO_3 over summer made up between approximately 26-32% of the total major ions. Over winter this dropped significantly to approximately 20% for W-2 to W-8 (Figure 4-6) (p-value < 0.05). At the largely hill-fed site W-1, the reduction was slightly less, falling to from 37% to 27% over winter (Figure 4-6) (p-value < 0.05). Na proportions changed little in the upper Waimea, from W-1 to W-4, but did decrease significantly between W-5 and W-8, dropping from approximately 18-21% over summer, to 15-16% over winter (Figure 4-6) (p-value < 0.05). Over winter there was a significant increase in SO_4 proportions, rising from approximately 2-3% over summer, to 8-10% over winter (Figure 4-6) (p-value < 0.05). Ca proportions also increased significantly over winter between W-4 and W-8, rising from approximately 16% over summer to approximately 20% over winter (Figure 4-6) (p-value < 0.05).

As a result of this, there was a shift in major water facie over winter in the Waimea Stream from W-2 through to W-8. W-1 remained with HCO_3-Na type water, with a reduction in Ca, while the remaining sites were all HCO_3-Ca type waters over winter (Figure 4-6).

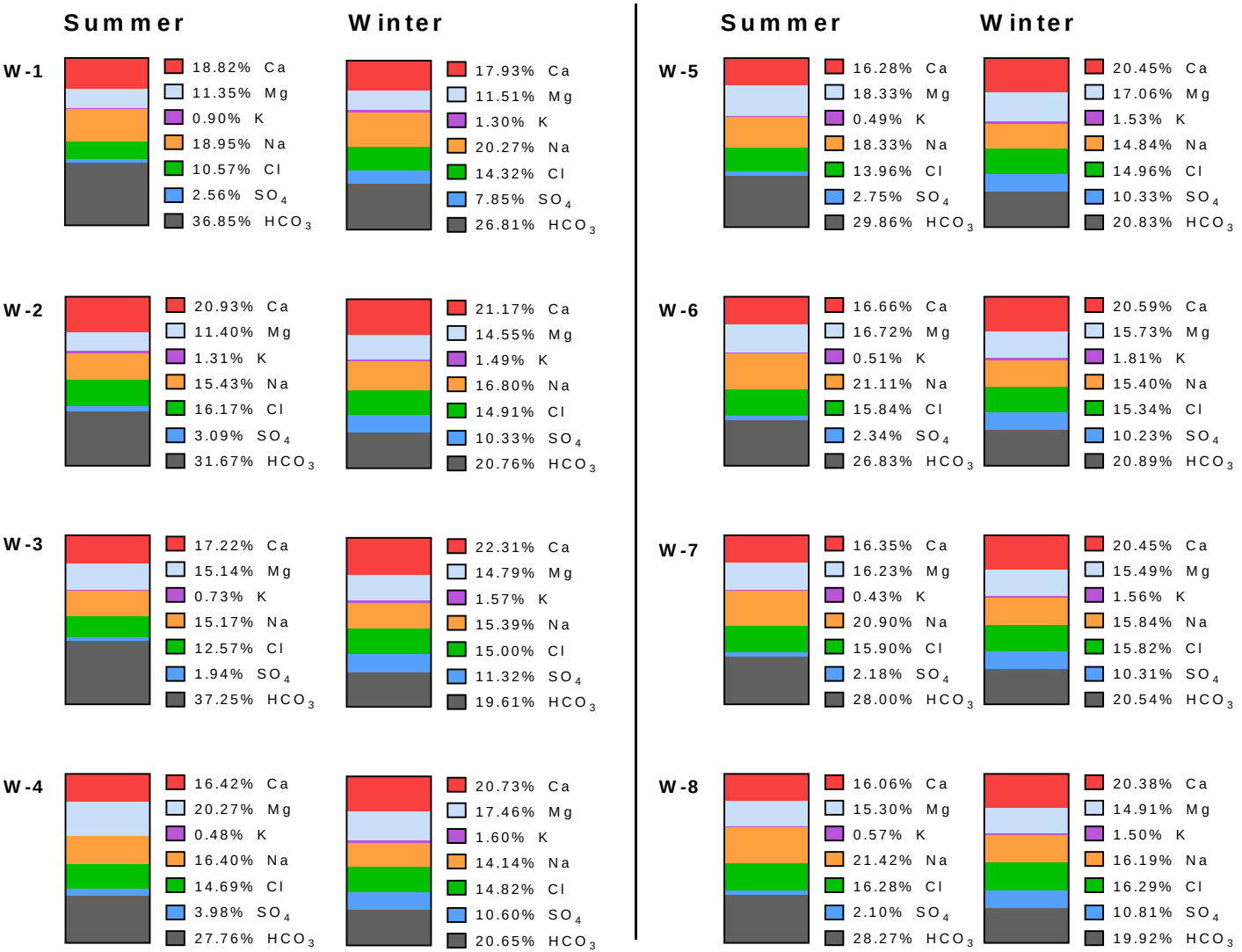

Figure 4-6 Waimea Stream summer vs winter major ion composition. Water samples were collected monthly from the Waimea Stream (W-1 to W-8) (for map see Figure 2-1) and were analysed for the major ions (Ca, Mg, K, Na, Cl, SO_4, HCO_3). Proportion charts of mean major ion composition between summer and winter for Waimea Stream are displayed. Summer major ion proportions are based on the means of February and March 2016 measurements while winter proportion are based on the means of June and July 2016 data.

Longridge ion proportions

During summer there were two distinct water facies in Longridge Stream (Figure 4-7). L-1 to L-3 had HCO_3-Ca type waters, while L-4 had HCO_3-Na type waters. Over winter all sites on Longridge Stream had HCO_3-Ca type waters.

Similarly to the Waimea Stream, in Longridge stream, the most notable shift was a significant decrease in HCO_3 proportions between summer and winter (Figure 4-7). For L-1 to L-3 this shift was greater than at L-4, dropping from approximately 40% over summer, to 20% over winter (Figure 4-7) (p-value < 0.05). At L-4, HCO_3 dropped from 29% over summer, to 20% over winter (Figure 4-7) (p-value < 0.05). SO_4 increased significantly from summer to winter in Longridge Stream, i.e. from approximately 1-2% to 11-12% respectively (Figure 4-7) (p-value < 0.05). Na had a similar pattern to that of the Waimea Stream, with no apparent shift in the upper catchment from L-1 to L-3, while there was a significant decline in the Na proportion at L-4, from 22% over summer to 16% over winter (Figure 4-7) (p-value < 0.05). There was no significant change in Ca proportions over winter compared to summer in Longridge Stream.

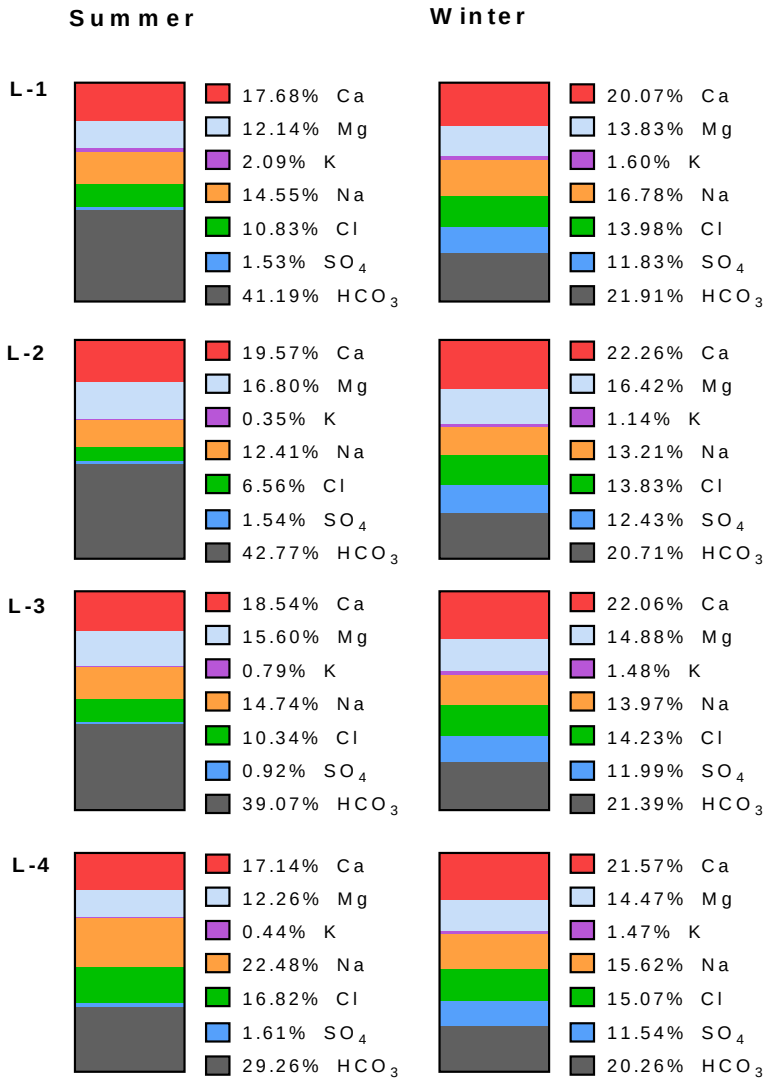

Figure 4-7 Longridge Stream summer vs Winter major ion composition. Water samples were collected monthly from the Longridge Stream (L-1,2,3,4) (for map see Figure 2-1) and were analysed for the major ions (Ca, Mg, K, Na, Cl, SO_4, HCO_3). Proportion charts based on the mean major ion composition between summer and winter for Longridge Stream. Summer major ion proportions are based on the mean of February and March 2016 measurements while winter proportions are based on the mean of June and July 2016 measurements.

Waimea Stream water quality

Temperatures decreased fairly steadily from February to July across all sites on both the Waimea and Longridge Stream (Figure 4-8 & Figure 4-9). Conductivity showed no apparent trend between February and July. Levels of pH for the Waimea Stream was highest over March and April and was generally above pH 7.0, while in July it was significantly lower than the previous five months (p-value < 0.05). Turbidity ranged from <0.5 to 14 FAU between February and June, while during July turbidity increased substantially to between 20 FAU at W-1 and 49 FAU at W-2 (Figure 4-8). There was much greater variation in dissolved oxygen during February, March and April (standard deviation >2.9 mg/L), compared to May, June and July (standard deviation <0.9 mg/L) (Figure 4-8 & Figure 4-9).

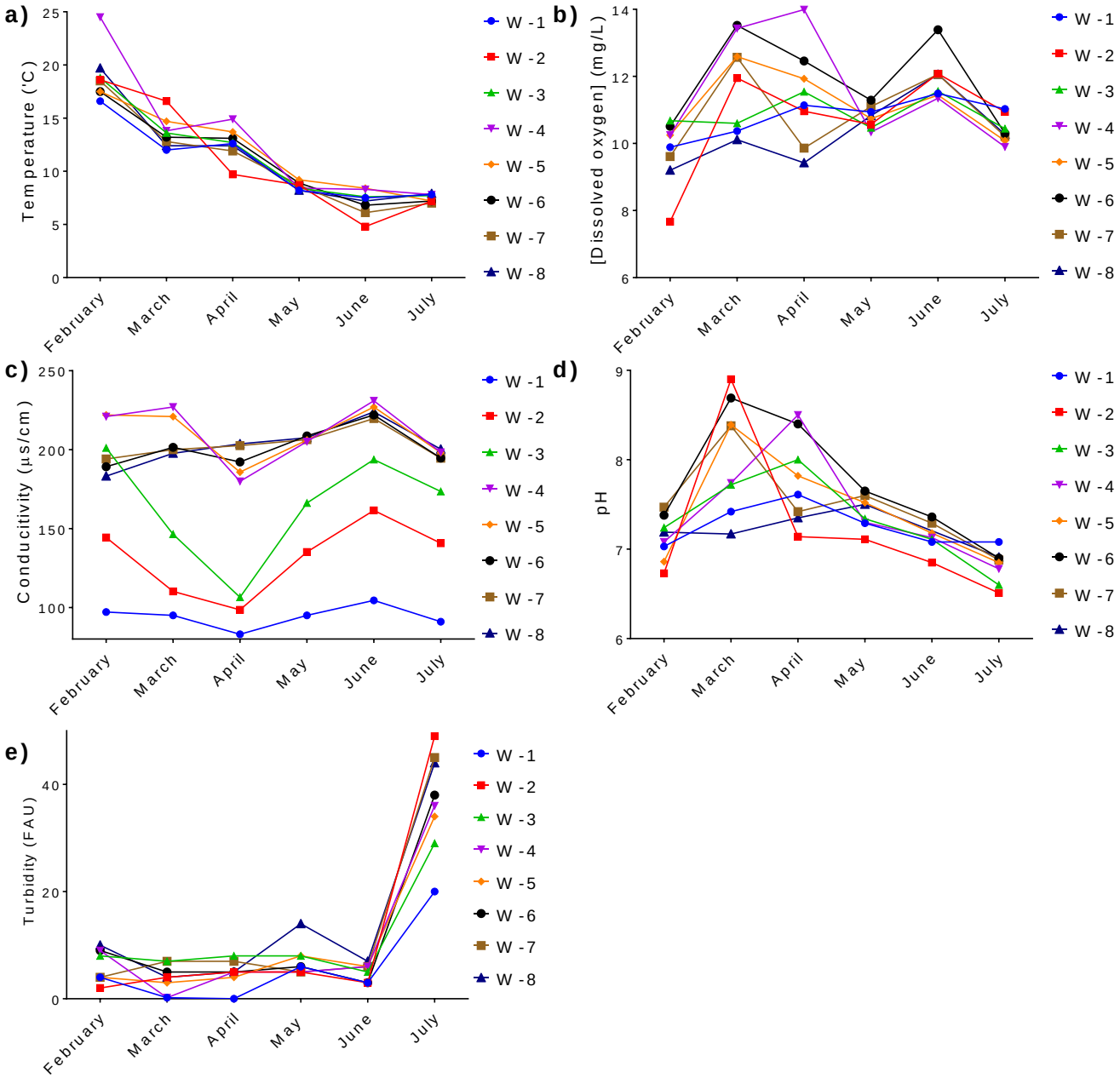

Figure 4-8 Monthly basic water quality of the Waimea Stream by site. Water quality was monitored monthly for six months for different sites along Waimea Stream (W-1 to W-8) (for map see Figure 2-1) and the **a)** temperature, **b)** dissolved oxygen, **c)** conductivity **d)** pH and e) turbidity were determined. Monthly data is displayed.

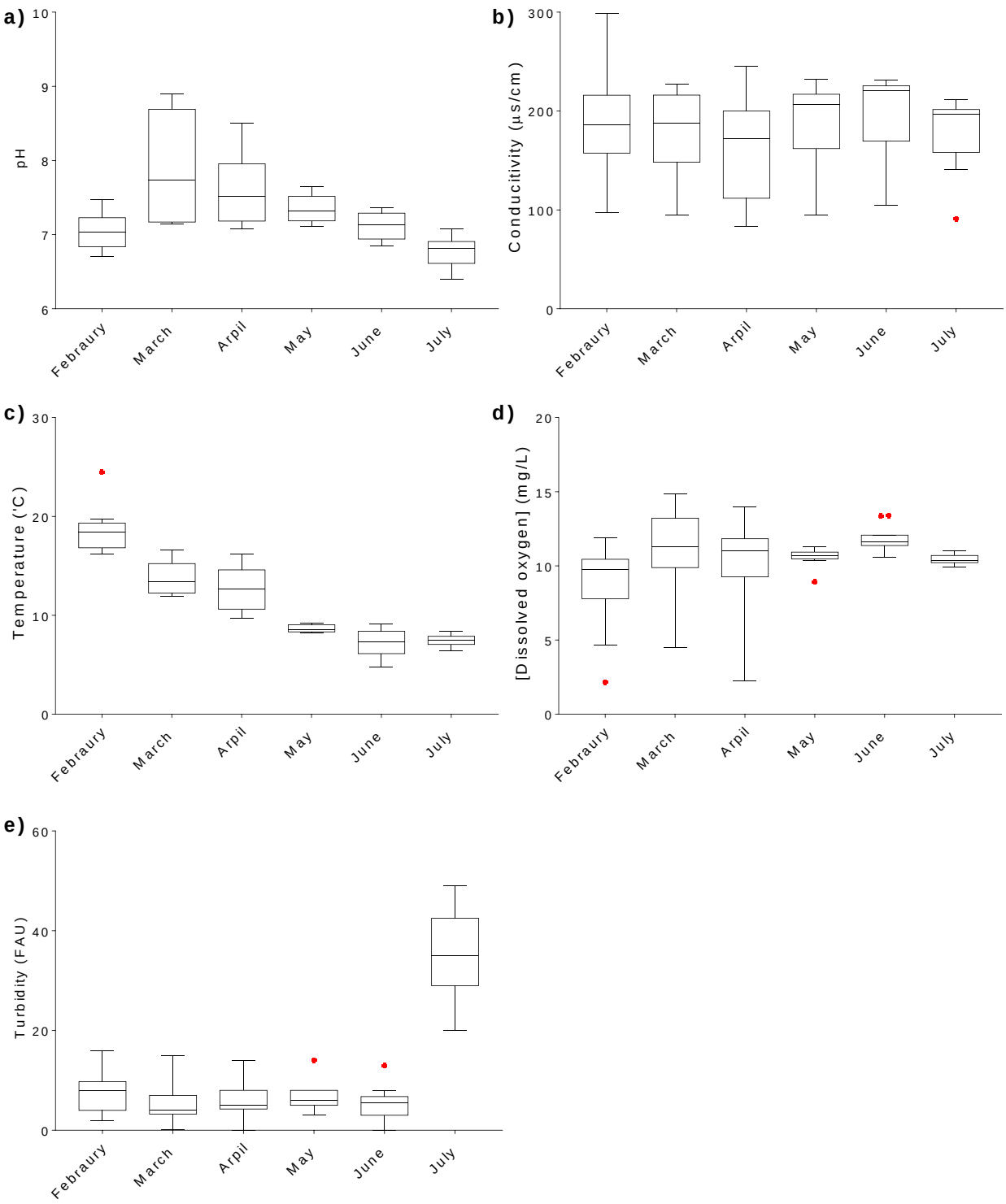

Figure 4-9 Monthly basic water quality of the Waimea Stream. Water quality was monitored monthly for six months for different sites along Waimea Stream (W-1 to W-8) (for map see Figure 2-1) and the a) temperature, b) dissolved oxygen, c) conductivity d) pH and e) turbidity were determined. Tukey plots with median and interquartile range from 8 measurements are shown for each month. Whiskers are 1.5X the interquartile range, red crosses are outliers.

Longridge Stream water quality

Longridge Stream temperatures between February and July declined significantly (Figure 4-10) (p-value < 0.05). Dissolved oxygen at L-2 between February and April was approximately 5 mg/L, which then rose significantly to approximately 10 mg/L from May through to July (Figure 4-10) (p-value < 0.05).

Conductivity increased significantly during the wetter months in the lower reaches (Figure 4-10) (p-value < 0.05). At L-3 and L-4 between February-April and May-July, conductivity increased from between approximately 150-180 µs/cm to 200-220 µs/cm. The pH in Longridge Stream was significantly higher during March and April at L-3, otherwise there was no apparent changes in pH at the remaining site between the months investigated. Turbidity was significantly elevated during July (p-value < 0.05), while during February to June it was consistently <18 FAU (Figure 4-10e).

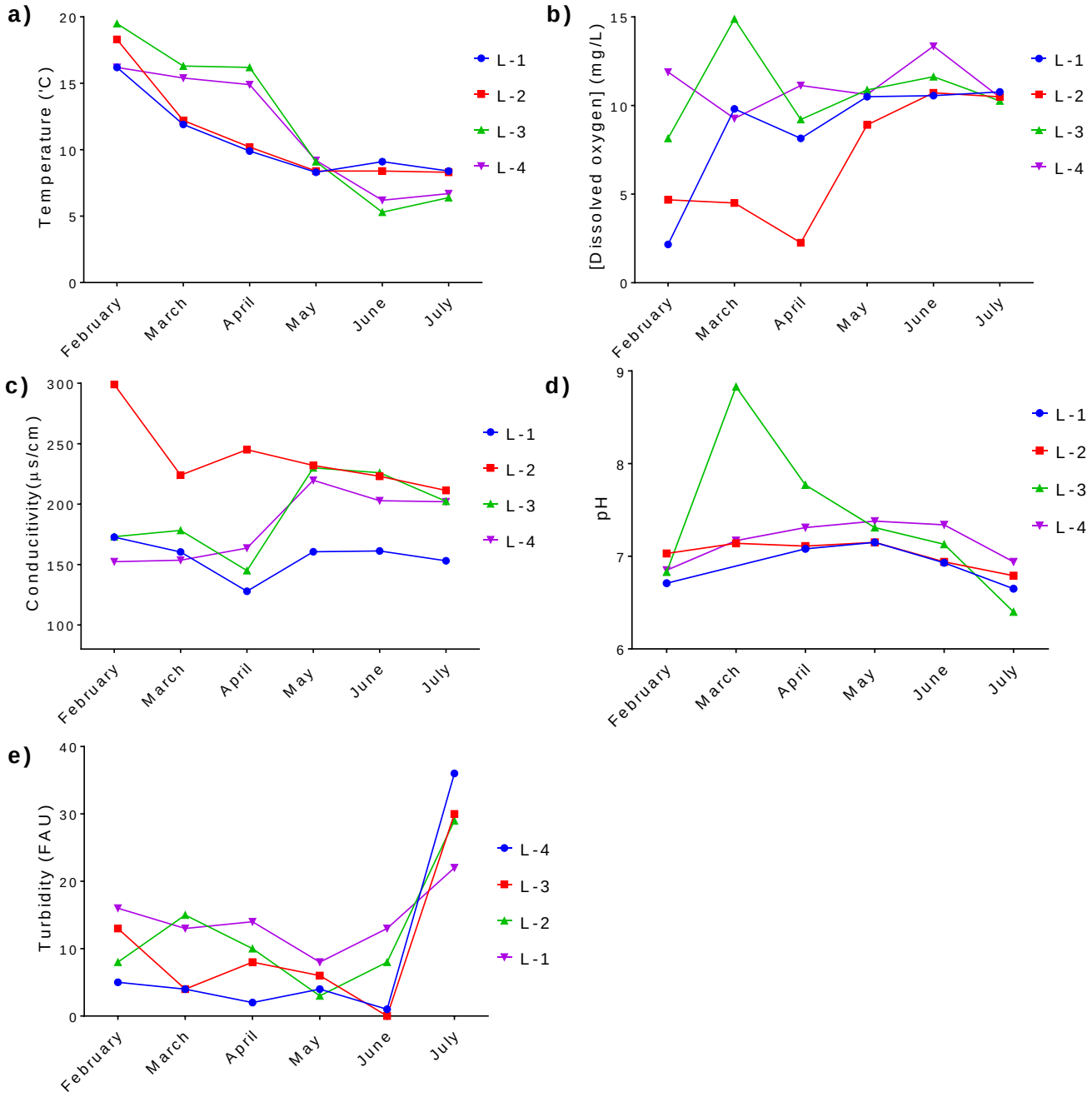

Figure 4-10 Monthly basic water quality of the Longridge Stream. Water quality was monitored monthly for six months for different sites along the Longridge Stream (L-1 to L-4) (for map see Figure 2-1), and the a) temperature, b) dissolved oxygen, c) conductivity d) pH and e) turbidity were determined.

Waimea Stream major ion chemistry

HCO_3 was particularly high during February, with concentrations from 51-70 mg/L for W-1, W-2 and W-6 to W-8, which dropped significantly to between 20-36mg in July (Figure 4-11) (p-value < 0.05). W-3 to W-5 had particularly high HCO_3 concentrations during February, ranging from 76 to 110 mg/L, which then dropped to comparable levels to all the other sites in July (Figure 4-11).HCO_3 was significantly higher during February than during July (p-value < 0.05) (Figure 4-12c). Na decreased steadily in the lower Waimea, at W-4 to W-8, from approximately 15-18 mg/L during February, to 9-10 mg/L during July (Figure 4-11). Na was significantly elevated during February and March compared to July (p-value < 0.05) (Figure 4-12d). Mg was significantly higher in the Waimea Stream from W-3 to W-8 during February compared to May and July (p-value < 0.05), the two months which had the greatest in-stream flow on the day of monitoring (Figure 4-12).

Concentrations of SO_4 increased significantly at (W-3,4,5,6,7,8), between February, which had concentrations of 3-7 mg/L, and July, which had concentrations of 16-18 mg/L. SO_4 was significantly higher during May, June and July (p-value < 0.05) (Figure 4-12b). K also increased at W-3 to W-8, from 0.4-0.7 mg/L during February, to 1.7-3.0 mg/L during July. K was significantly higher during May, June and July compared to February and March (p-value < 0.05) (Figure 4-12f). Ca did not appear to show a significant difference between the low summer flows of February and the high flow conditions of July (Figure 4-12).

Overall, HCO_3, Na, and Mg concentrations were higher during summer, while SO_4 and K concentrations were higher during winter.

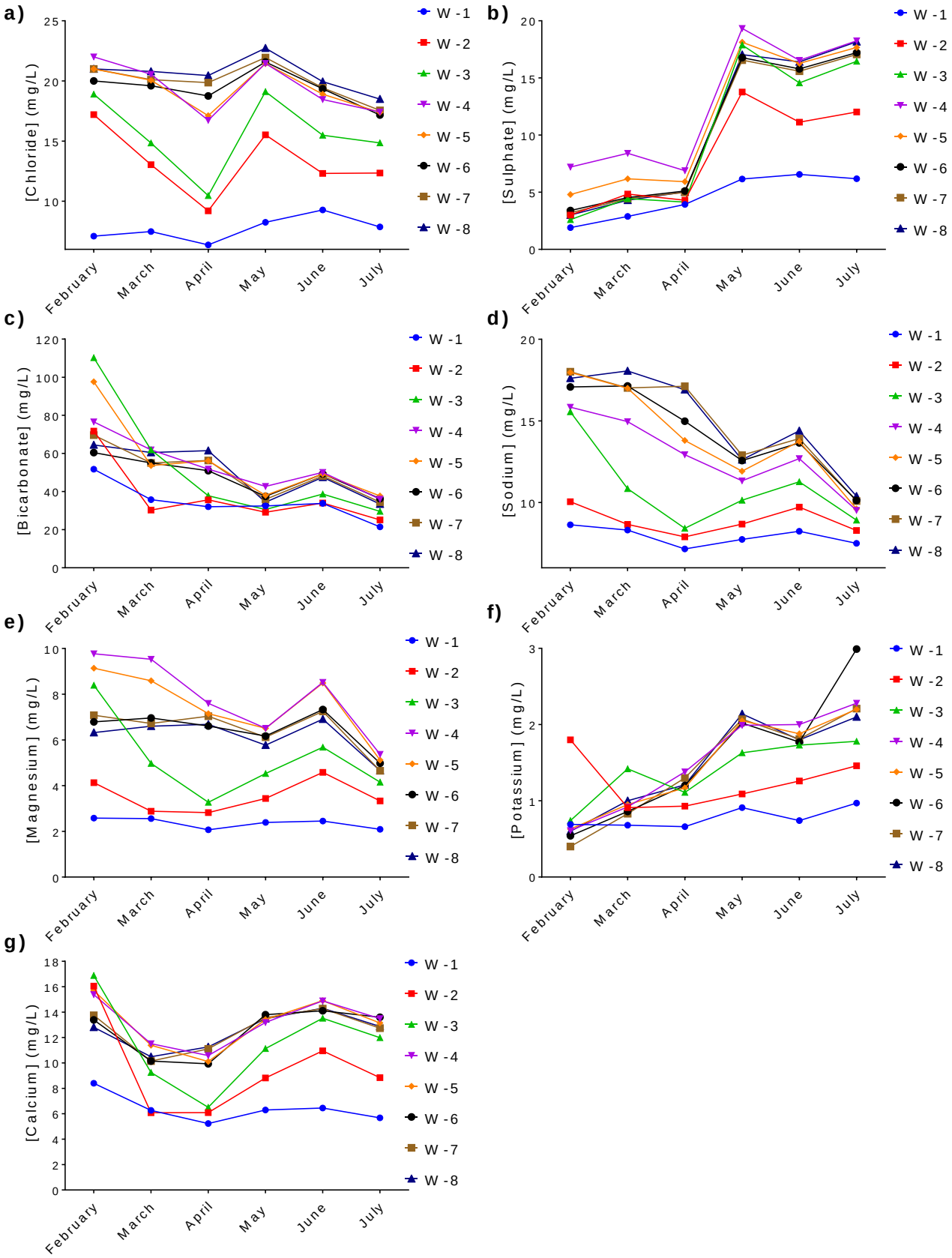

Figure 4-11 Temporal major ion chemistry of Waimea Stream by site. Water samples were collected monthly from the Waimea Stream (W-1 to W-8) (for map see Figure 2-1) for six months and were analysed for a) chloride, b) sulphate, c) bicarbonate, d) sodium, e) magnesium, f) potassium, and g) calcium.

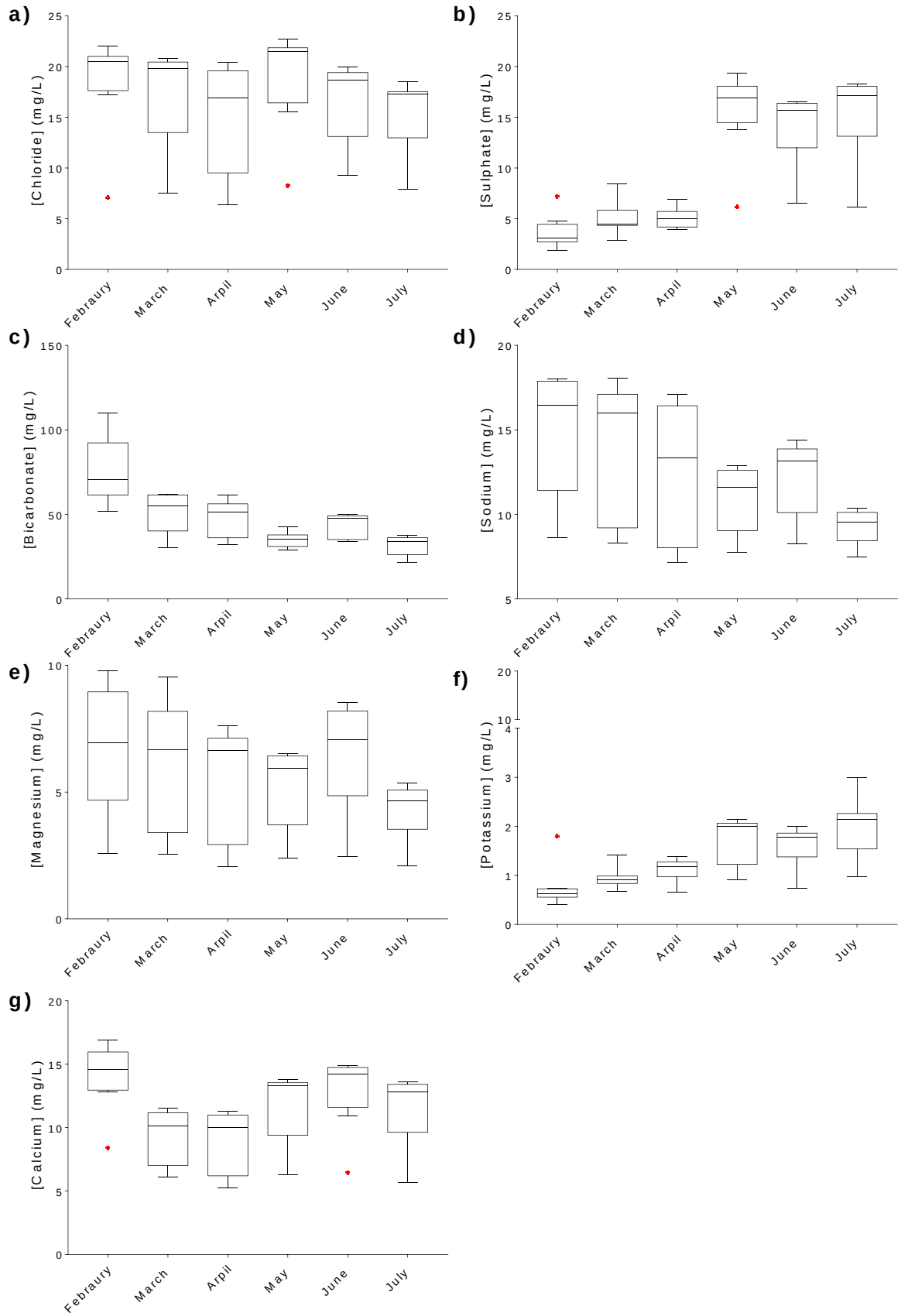

Figure 4-12 Temporal major ion chemistry of Waimea Stream. Water samples were collected monthly from the Waimea Stream (W-1 to W-8) (for map see Figure 2-1) for six months and were analysed for a) chloride, b) sulphate, c) bicarbonate, d) sodium, e) magnesium, f) potassium, and g) calcium. Tukey plots with median and interquartile range from 8 measurements are shown for each month. Whiskers are 1.5X the interquartile range, red crosses are outliers.

Waimea stream trace element chemistry

Overall, Mn concentrations were significantly higher during February when compared to April and May (p-value < 0.05), while there was no significant variation in Fe (Figure 4-14). The concentration of Fe and Mn were particularly high in February at W-3, with concentrations of 750 µg/L and 102 µg/L respectively. At W-3, Fe dropped gradually to 120 µg/L in May, whereas Mn decreased rapidly to 30 µg/L in March and was then steady through to July. W-2 had high Mn concentrations in February which also dropped to 6.1 µg/L in March. W-1 had Fe concentrations of approximately 300 µg/L for February to March, which then dropped to 72 µg/L in July (Figure 4-13).

Al concentrations were significantly higher during July in the lower Waimea (W-3 to W-8), with concentrations of approximately 100-150 µg/L, compared to concentrations of less than 50 µg/L during the previous five months (p-value < 0.05)(Figure 4-14). B concentrations for W-4 to W-8 were significantly higher during May to June compared to March and April (p-value < 0.05), rising from approximately 15-20 µg/L to 25-30 µg/L (Figure 4-13).

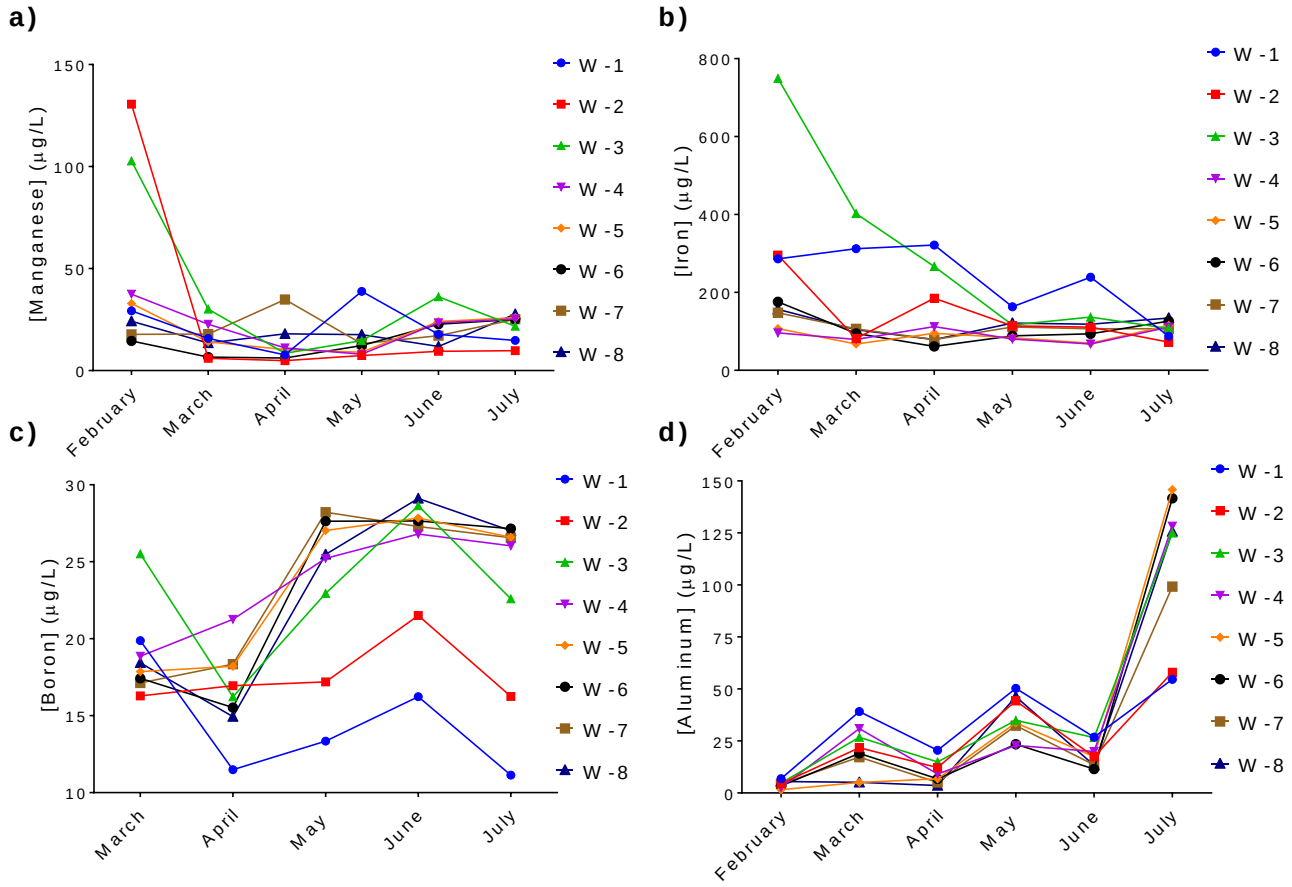

Figure 4-13 Temporal chemistry of Waimea Stream by site. Water samples were collected monthly from Longridge Stream (L-1 to L-4) (for map see Figure 2-1) for six months and were analysed for a) manganese, b) iron, c) boron, d) aluminium. Here monthly data for each site is displayed. No data for boron was collected during February.

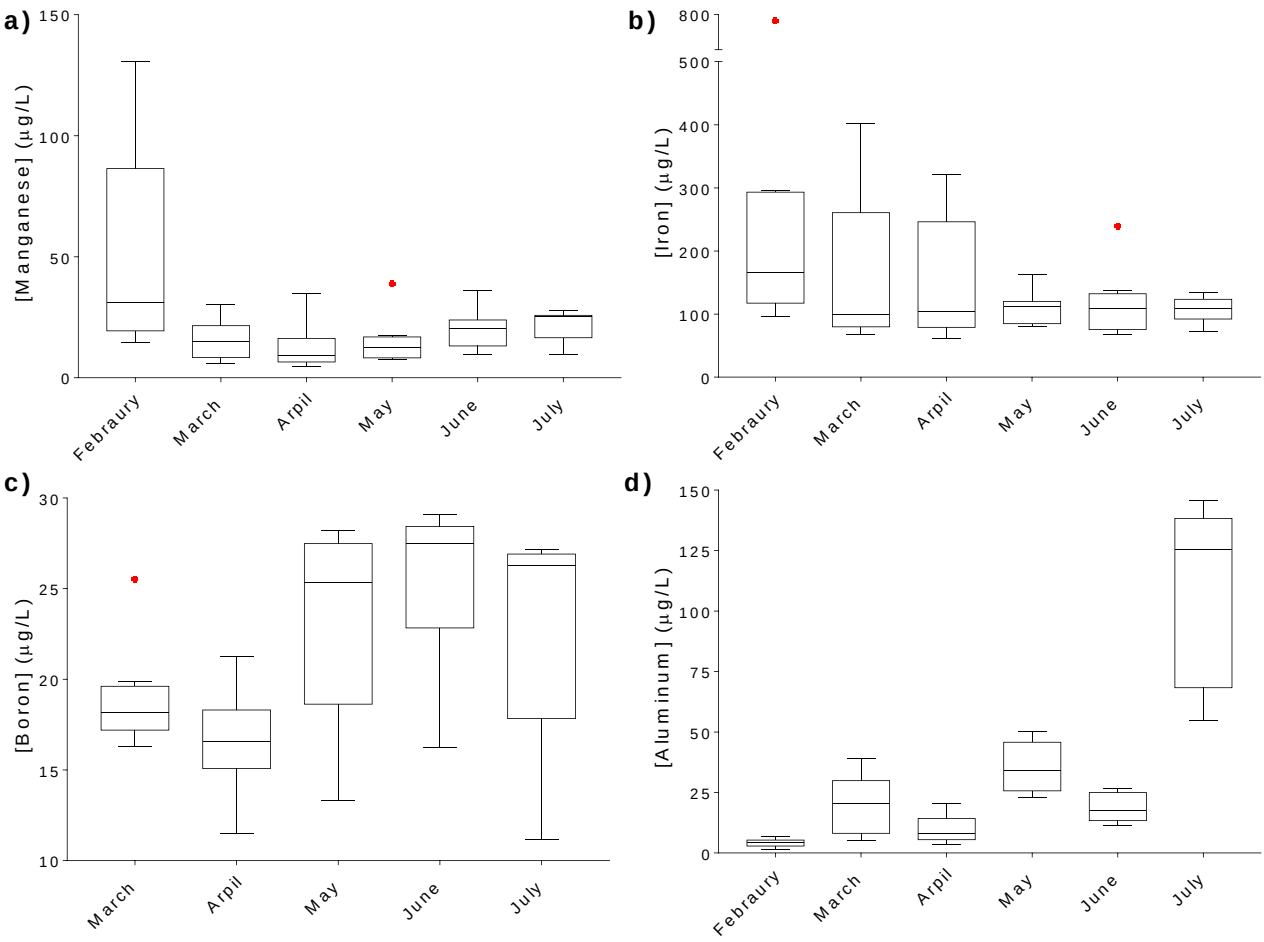

Figure 4-14 Temporal chemistry of Waimea Stream. Water samples were collected monthly from Longridge Stream (L-1 to L-4) (for map see Figure 2-1) for six months and were analysed for a) manganese, b) iron, c) boron, and d) aluminium. Tukey plots with median and interquartile range from 8 measurements are shown for each month. Whiskers are 1.5X the interquartile range, red crosses are outliers. No data for boron was collected during February.

Longridge Stream chemistry

HCO_3 and Na decreased significantly between February and July (p-value < 0.05). SO_4 increased significantly during May, June and July. The April sample taken at L-3 had highly elevated concentrations of Cl, K and SO_4. As a point of comparison, K was four times greater at L-3 than at L-2, Cl two times that of L-2, and SO_4 six time greater than at L-2 during April (Figure 4-15).

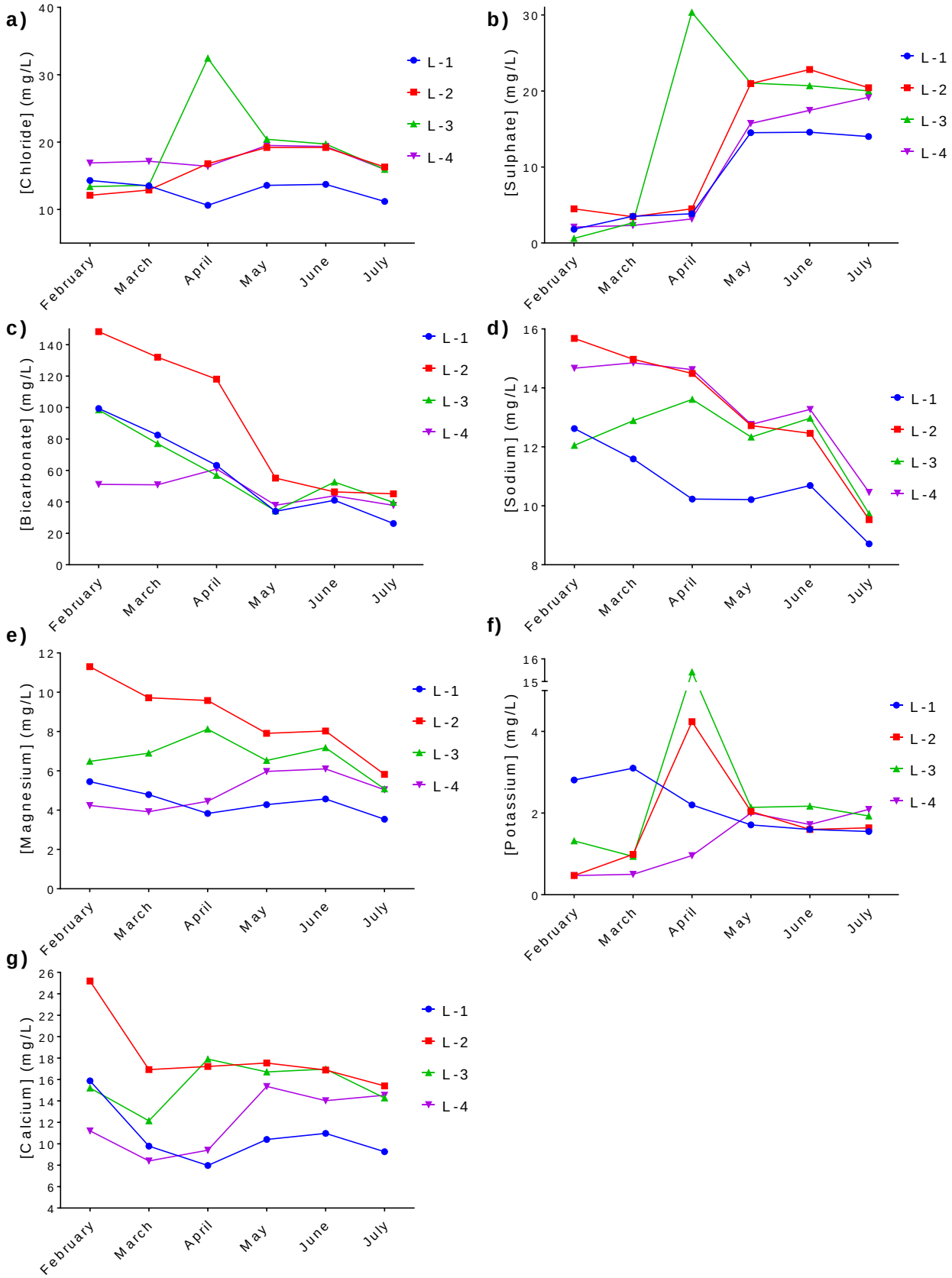

Figure 4-15 Temporal major ion chemistry of Longridge Stream. Water samples were collected monthly from Longridge Stream (L-1 to L-4) (for map see Figure 2-1) for six months and were analysed for a) chloride, b) sulphate, c) bicarbonate, d) sodium, e) magnesium, f) potassium, and g) calcium.

Longridge Stream trace elements

L-1, L-2 and L-3 all had elevated Fe and Mn during February, which declined to significantly lower concentrations by April and May (p-value < 0.05). The concentration of Al was significantly elevated during July (p-value < 0.05), which was the month with the highest in-stream flow at the time of sampling.

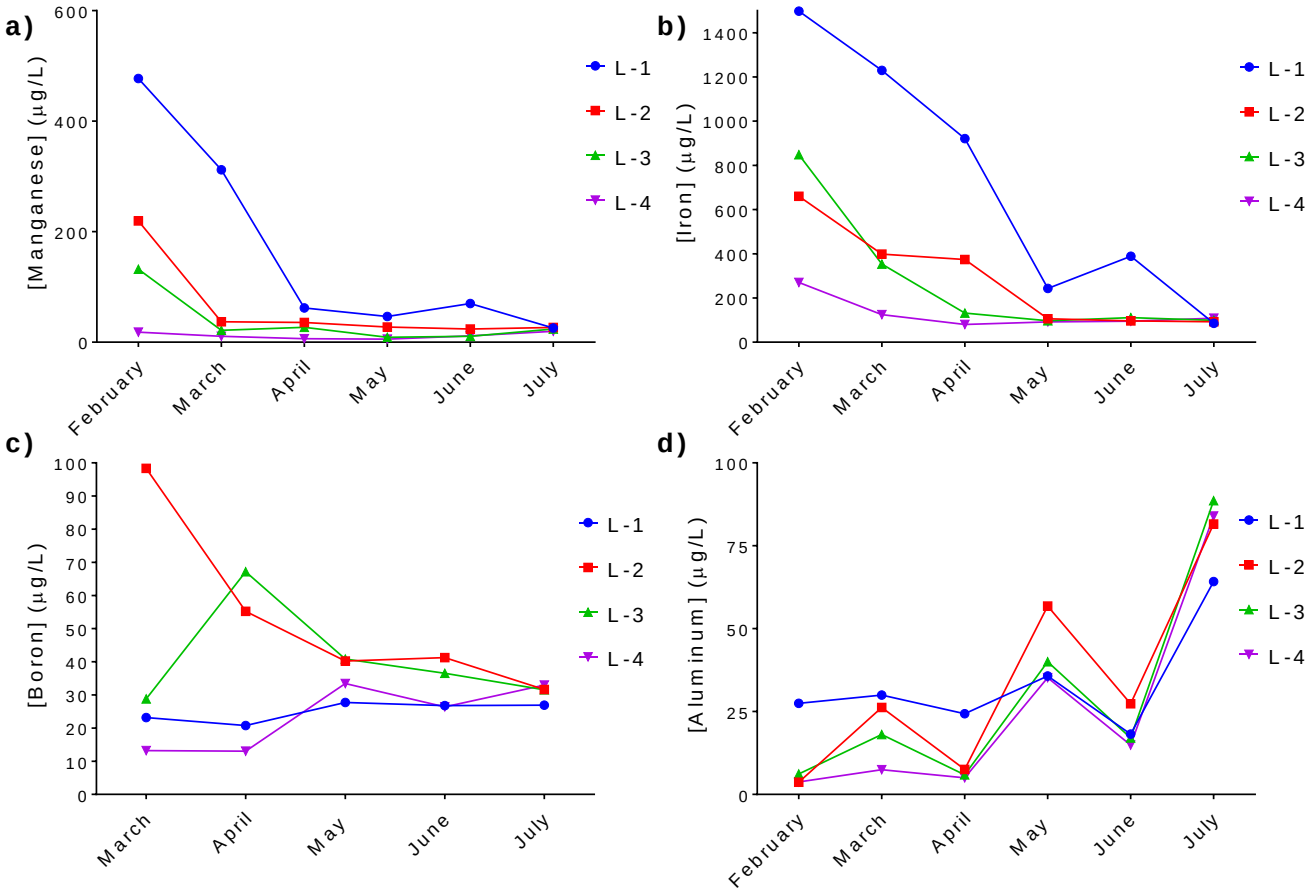

Figure 4-16 Temporal trace metal chemistry of Longridge Stream. Water samples were collected monthly from Longridge Stream (L-1 to L-4) (for map see Figure 2-1) for six months and were analysed for a) manganese, b) iron, c) boron, d) aluminium.

4.2.4. Marine aerosol ion ratios

In this section the ion ratios of Na:Cl and SO_4:Cl were investigated in relation to the respective marine aerosol ratio of each. The Na:Cl ratio was significantly elevated during February to April relative to May and July (Figure 3-17) (p-value < 0.05). During May and July the Na:Cl ratio approximated the marine aerosol ratio. Conversely, during February to April the SO_4:Cl ratio approximated the marine aerosol ratio, while during May to July SO_4 concentrations were significantly elevated relative to Cl (Figure 4-17).

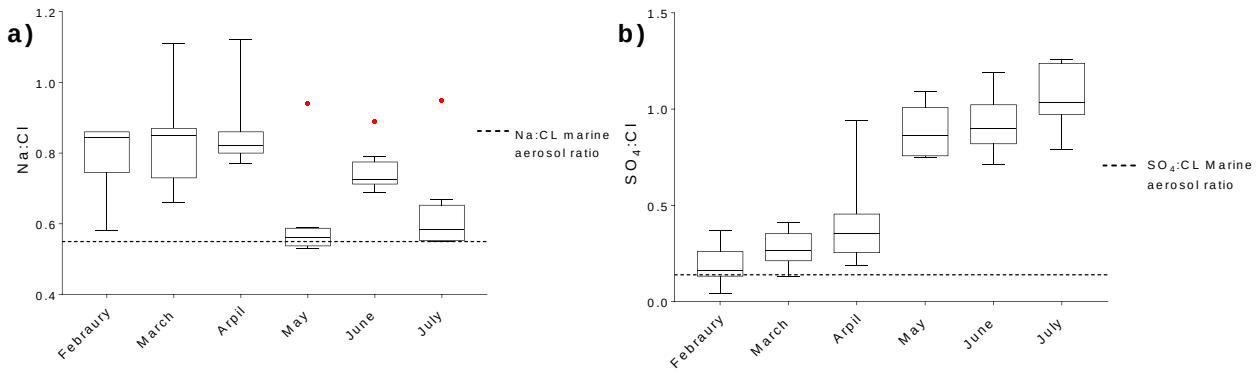

Figure 4-17 Major ion ratios of sodium and sulphate to chloride. Water samples were collected monthly from Waimea (W-1 to W-8) Longridge Stream (L-1 to L-4) (for map see Figure 2-1) for six months and were analysed for sodium, chloride and sulphate. Here monthly recorded ion ratios of a) sodium:chloride and b) sulphate to chloride are displayed. The marine aerosol ratio of Na:Cl and SO_4:Cl is displayed.

4.3. Nutrients

In this section nutrient concentrations were analysed both spatially and temporally. In order to establish differences between summer and winter, data collected during February and March has been contrasted with June and July. For the purposes of seasonal comparisons, the upper Waimea Stream (W-1 to W-3) has been contrasted with the lower Waimea Stream (W-4 to W-8).

4.3.1. Spatial variation in nutrients

Nitrate

There was a significant increase of nitrate concentrations from W-3 to W-4 on the Waimea Stream (p-value < 0.05) (Figure 4-18a). From W-3 to W-4, median nitrate concentrations increased from 0.7 mg/L to 3.5 mg/L. From W-4 downstream to W-8 median nitrate concentrations remained elevated at approximately the same concentration as W-4. At these five sites of the lower Waimea Stream, nitrate recorded concentrations of nitrate remained consistently elevated above approximately 2 mg/L. W-2 and W-3 had a greater range of nitrate concentrations, from > 3 mg/L to < 0.05 mg/L. W-1 had overall significantly lower nitrate concentrations than the rest of the Waimea Stream)p-value < 0.05), with a median concentration of 0.16 mg/L, and a maximum of 1.5 mg/L (Figure 4-18a).

Seasonally, nitrate concentrations in the upper Waimea Stream (W-1 to W-3) were very low during summer, with a median concentration of 0.015 mg/L, whereas in the lower Waimea Stream (W-4 to W-8), summer median nitrate concentrations were significantly higher at 2.6 mg/L (p-value < 0.05) (Figure 4-18c). During winter, nitrate concentrations were elevated in both the upper and lower Waimea when compared to their respective summer concentrations, with median nitrate concentrations of 1.5 mg/L and 4.0 mg/L respectively (p-value < 0.05) (Figure 4-18c).

Longridge Stream had a significant increase in nitrate concentration between the headwater sites (L-1 and L-2), which had median nitrate concentrations of approximately 0.8 mg/L to L-4, which had a median nitrate concentration of 3.3 mg/L (p-value < 0.05) (Figure 4-18a). Seasonally, Longridge Stream had significantly lower nitrate concentration over summer, with a median of 0.7 mg/L, compared to during winter where the median nitrate concentration was 3.8 mg/L (Figure 4-18c).

Dissolved reactive phosphorus

There was little variation in DRP concentrations between sites on the Waimea Stream, apart from between W-2, and W-3 of the Waimea Stream, where there was a significant increase from W-2 (median DRP concentration of 10.8 µg/L), to W-3 (median DRP concentration of 24.9 µg/L) (p-value < 0.05) (Figure 4-18b). DRP concentrations on Longridge Stream were significantly higher in the headwaters at L-2, compared to the other headwater site, L-1 (p-value < 0.05) (Figure 4-18b).

Seasonally, DRP concentrations in both the upper and lower Waimea Stream were significantly higher over winter (p-value < 0.05) (**Figure 4-18**d). This increase over winter was greater in the lower Waimea Stream. In the upper Waimea Stream, median DRP concentrations increased from a median of 12.1 µg/L during summer to 17.3 µg/L during winter, while in the lower Waimea Stream, it increased from 33.7 µg/L to 84.9 µg/L. In Longridge Stream, there was no apparent difference between summer and winter DRP concentrations, with summer DRP concentrations having a median concentration of 54 µg/L, while during winter it was 40.2 µg/L (Figure 4-18d).

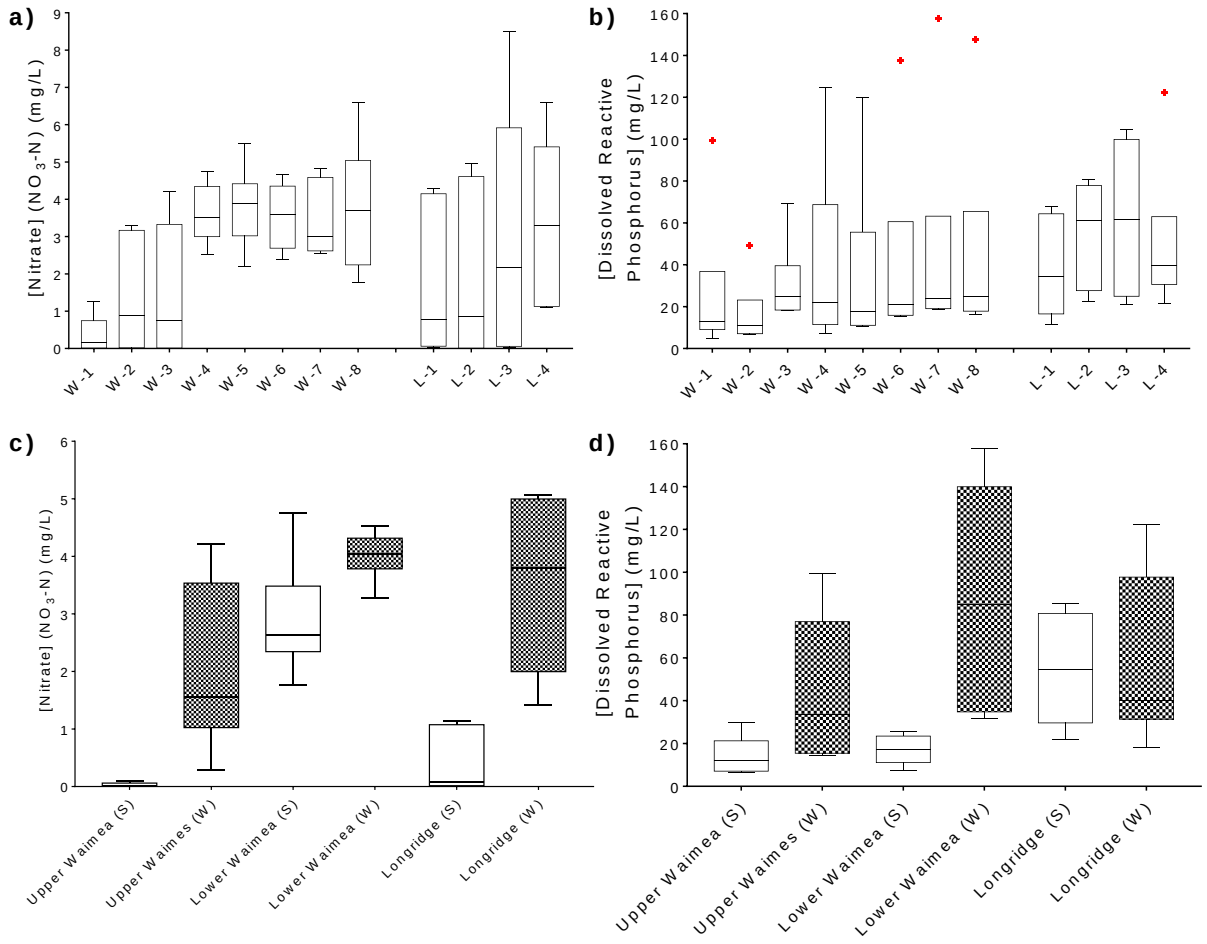

Figure 4-18 Nutrient levels in Waimea and Longridge Streams. Water samples were collected monthly from the Waimea Stream (W-1 to W-8) and from Longridge Stream (L-1 to L-4) (for map see Figure 2-1) for six months and were analysed for (a,c) nitrate (NO3-N) and (b,d) DRP. Tukey plots with median and interquartile range from six measurements at each site are shown for a) nitrate and b) DRP. The nutrient levels between summer (S-clear boxes, February-March data) and winter (W-shaded boxes-June-July data) of c) nitrate and d) DRP for the upper Waimea (W-1-3) and lower Waimea (W-4-8) as well as for Longridge Stream (L-1-4) is displayed.

4.3.2. Temporal variation of nutrients

Nitrate

Monthly nutrient concentrations recorded have been plotted for both the Waimea and Longridge Streams (see Figure 4-19). Concentrations of nitrate at W-1 to W-3 were low during February to April (<0.5 mg/L), before rising to higher concentrations during May, June and July. In contrast, further downstream, i.e., from W-4 to W-8, nitrate was elevated throughout the study period from February to July (>2.0 mg/L). Nitrate concentrations at W-1 showed less of an increase towards winter, only reaching 1.27 mg/L in July, compared to between 3.3-4.5 mg/L at the other sites of Waimea Stream.

Longridge Stream at L-1, L-2 and L-3 had a similar pattern to the upper Waimea, with low nitrate concentration (<0.2 mg/L) during February and March, and elevated nitrate during May, June and July (Figure 4-19a,b). Longridge Stream at L-4 however had slightly yet significantly elevated nitrate concentration during February to March (>1.0 mg/L) compared to the upper Longridge catchment (<0.2 mg/L) (p-value>0.05).

Dissolved reactive phosphorus

DRP concentrations in the Waimea Stream and Longridge Stream at L-4 increased significantly during July at all sites (Figure 3-18c,d). In Longridge Stream however, DRP concentrations at L-1 to L-3 during February and April were similar to DRP concentrations during July, with no statistically significant difference between these three months.

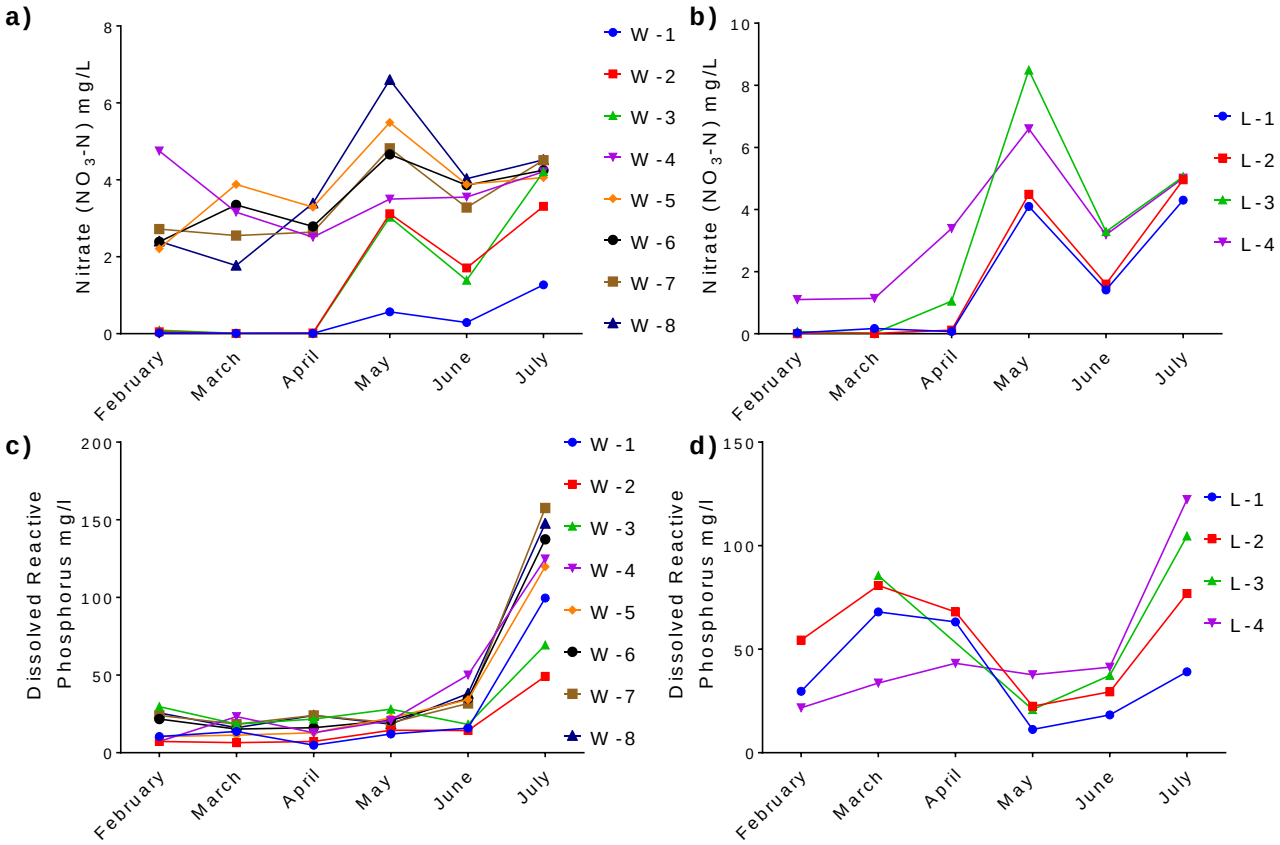

Figure 4-19 Monthly nutrients levels in Waimea and Longridge Streams. Water samples were collected monthly from the Waimea Stream (W-1 to W-8) and from Longridge Stream (L-1 to L-4) (for map see Figure 2-1) for six months and were analysed for (a,b) nitrate (NO_3-N) and (c,d) dissolved reactive phosphorus.

4.4. Sediment chemistry

In this section the sediment chemistry for a suite of major ions as well as trace elements were investigated for each site along both the Waimea and Longridge Streams. The data was plotted against the sites distance from the Waimea/Mataura confluence (Figure 4-20a,h).

Waimea Stream sediment chemistry

For statistical purposes, sediment concentrations measured at sites of the upper Waimea Stream (W-1-W-5) were grouped and contrasted to those obtained from the lower Waimea (W-6-W-8).

Ca, Mg, Mn, Cu, Co, Ni, and Va increased significantly over the roughly 4 Km between W-5 and W-6(Figure xy). Mn for example increased from 3000 µg/g at W-5 to 12000 µg/g at W-6, Co from 16 µg/g to 45 µg/g, Cu from 14 µg/g to 25 µg/g (p-value < 0.05) (Figure 4-20). Na rose more steadily from W-2 to W-5.

There was a significant spike in a series of elements at W-3 including Sb, K, Zn, Mo, B and Nb For example, Zn was 85 µg/g at W-2 and W-4, and then was 140 µg/g at W-3. Sb sediment concentrations were 0.06 µg/g at W-3, while being half this at W-2 and W-4 (Figure 4-20).

Longridge Stream sediment chemistry

There were no obvious trends for Longridge Stream for most of the elements analysed. The majority of elements appeared to increase between L-2 and L-4, however, levels at L-4 were generally quite comparable to those at L-1 (see Figure 4-21).

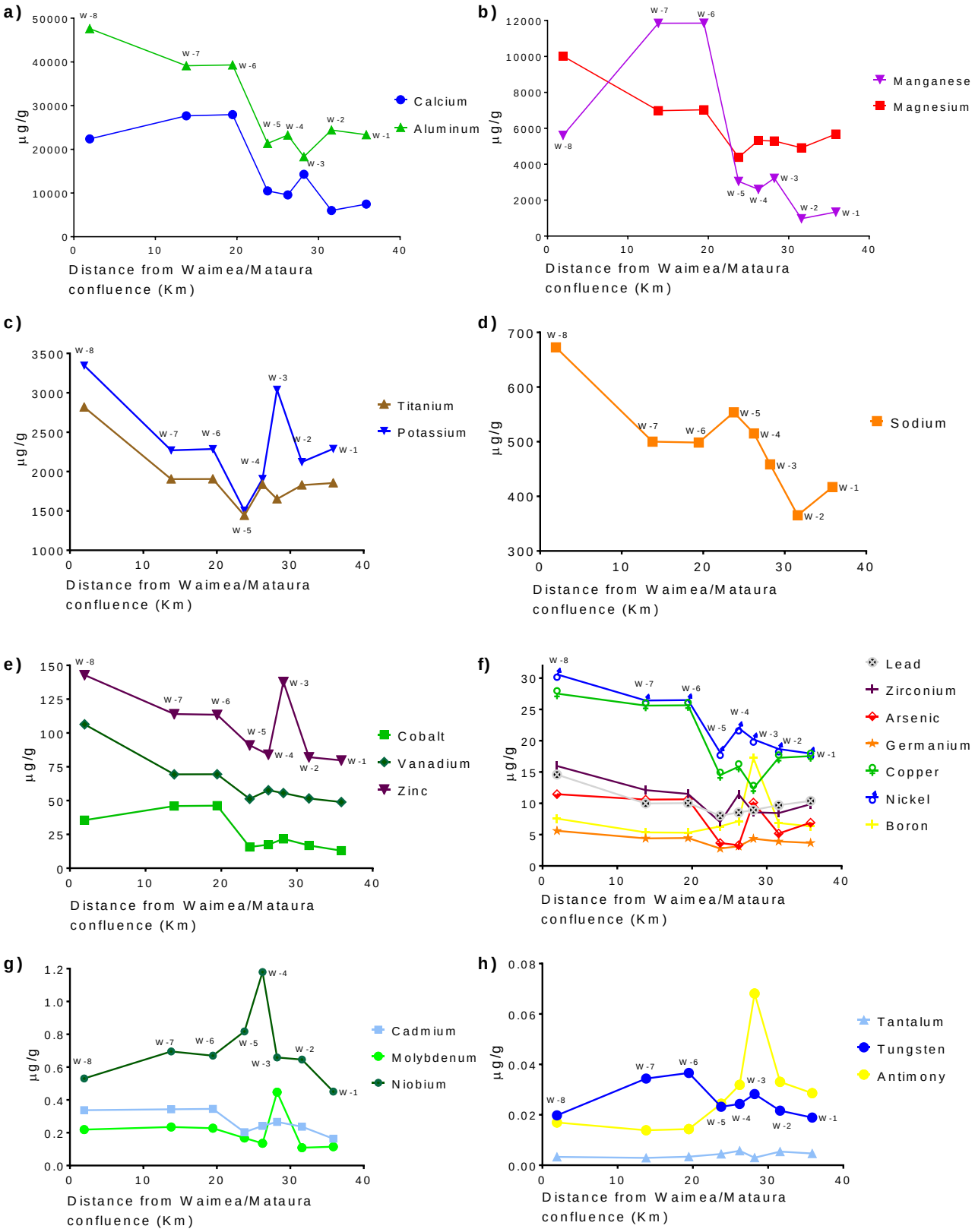

Figure 4-20 Waimea Stream sediment chemistry. Grab samples of sediment were obtained at sites W-1 to W-8 on Waimea Stream (for map see Figure 2-1) during February. The sediment was dried, sieved to 63 µm and digested with acid. Samples were then analysed with ICP mass spectrometry for a) Ca, Mg, b) Mn, Mg, c) Ti, K, d) Na, e) Co, V, Zn, f) Pb, Zr, As, Ge, Cu, Ni, B, g) Cd, Mo, Nb, h) Ta, W, Sb. Sediment composition is displayed as µg/g of dry sediment (<63 µm).

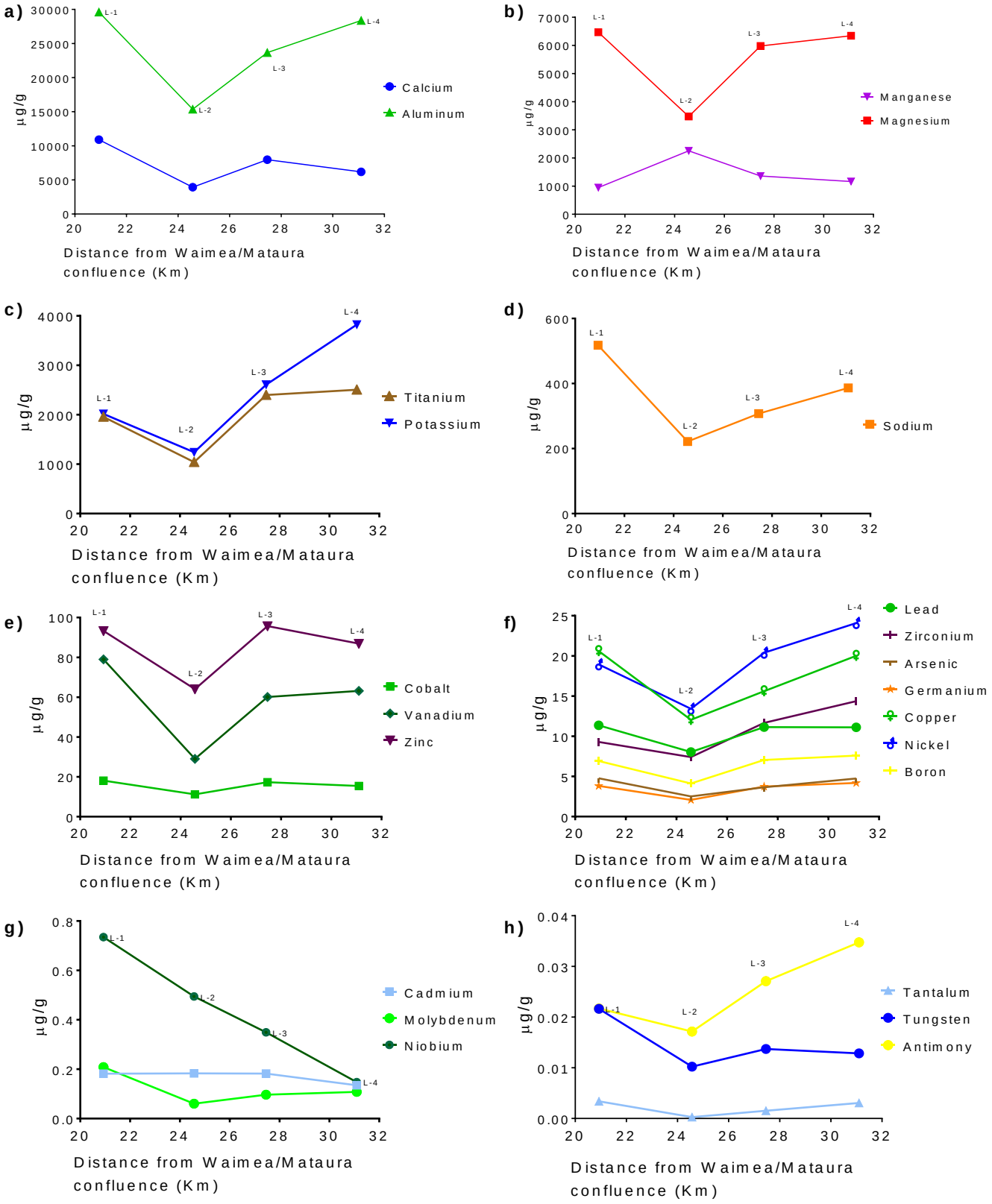

Figure 4-21 Longridge Stream sediment chemistry. Grab samples of sediment were obtained at sites L-1 to L-4 on Longridge Stream (for map see Figure 2-1) during February. The sediment was dried, sieved to 63 µm and digested with acid. Samples were then analysed with ICP mass spectrometry for a) Ca, Mg, b) Mn, Mg, c) Ti, K, d) Na, e) Co, V, Zn, f) Pb, Zr, As, Ge, Cu, Ni, B, g) Cd, Mo, Nb, h) Ta, W, Sb. Sediment composition is displayed as µg/g of dry sediment (<63 µm).

4.5. Stable isotopes

In this section the stable isotopes of hydrogen, oxygen and carbon were utilised to elucidate the sources and flow paths of water across the Waimea Plains. Analysis was carried out both between different reaches of the Waimea Stream, and between different seasons. Isotopic compositions for precipitation across Southland were used to aid in identifying the source of water to the Waimea Plains aquifer and surface waters. Isotopic data from the Oreti River was also analysed to determine whether there was any inter catchment transfer between the Oreti River and the Waimea Plains aquifer and surface waters. The stable isotope composition of carbon was then investigated for evidence of connectivity between the Waimea Plains groundwater and the Waimea Stream. In this section the data is interpreted as it is presented.

4.5.1. Oxygen and hydrogen stable isotopes

The isotopic composition of coastal rainfall at Invercargill and Riverton, inland rainfall from Queenstown and Roxburgh, along with the isotopic composition of rainfall on the Waimea Plains was used as a reference point for the surface waters of the Waimea Plains (for map see Figure 4-22). Rainfall data was thus used to indicate whether the ground and surface water of the Waimea Plains was from local or distal sources. The Oreti River is a large main stem alpine fed river that runs past the north-western edge of the Waimea Plains. There is very little relief between the Waimea Plains and the Oreti River. There is evidence of an historic flood channel of the Oreti River across the Waimea Plains which has led to speculation that the Oreti River may still be hydrologically connected to the Waimea Plains aquifer (Mcintosh et al., 1998). Oreti River along with Balfour and Riverton rainfall data, has been collected by Environment Southland (D. May, personal communication, 20th August 2016). Queenstown, Roxburgh and Invercargill rainfall data has been collected by the Department of Chemistry, University of Otago (R. Frew, personal communication, 22nd August 2016).

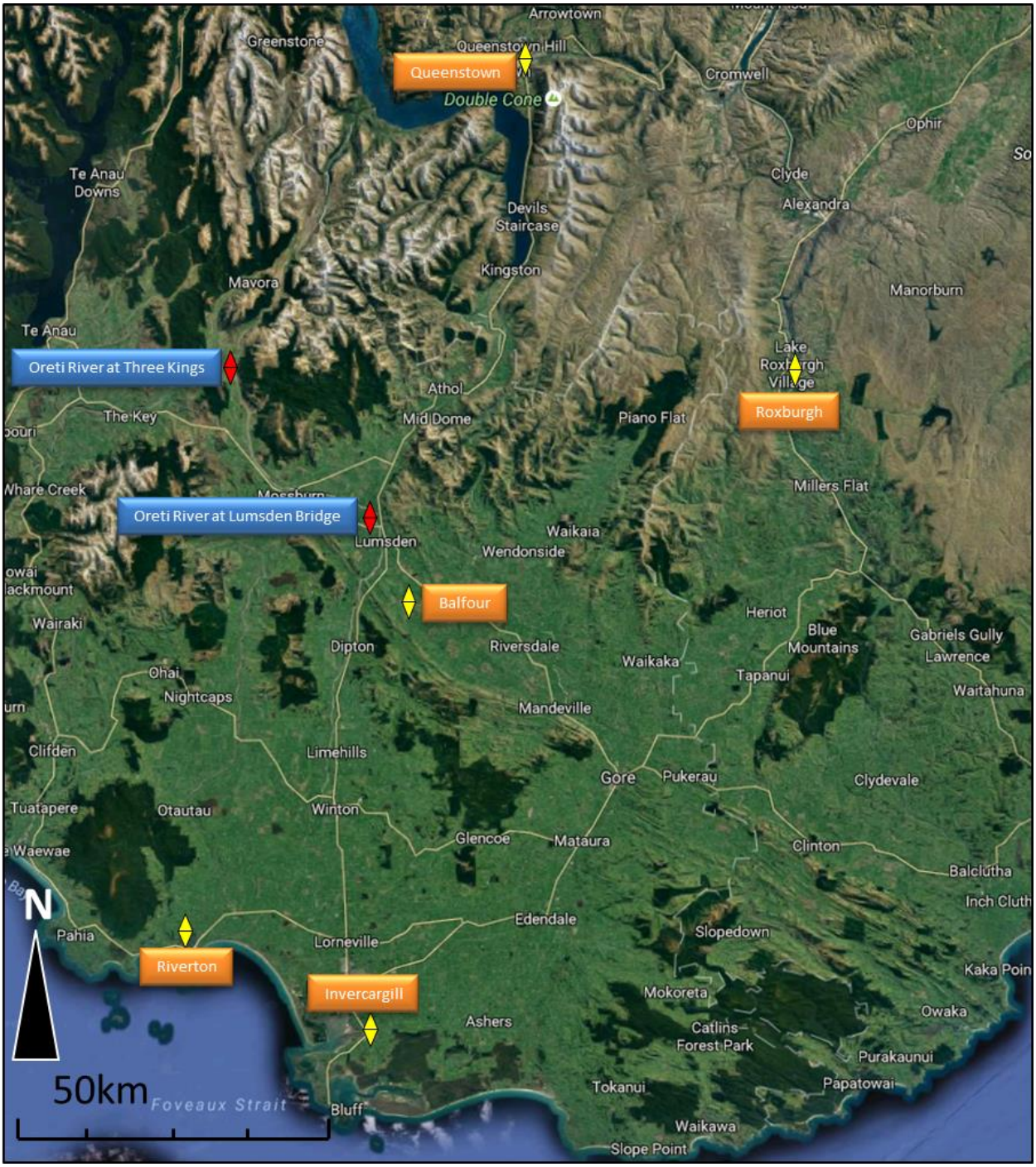

Figure 4-22 Precipitation and Oreti River stable isotope monitoring sites. Precipitation sites: yellow diamonds, Oreti River sites: Red diamonds. Riverton and Invercargill are coastal precipitation sites (<20 km inland from the south coast). For the remaining precipitation sites, distance from the south, east and west coast of New Zealand is noted in brackets. Balfour (S-70 km, E-100 km, W-150 km), Queenstown (S-160km, E-170 km, W- 100km), Roxburgh (S-130 km, E-90 km, W-180 km). Balfour and Riverton precipitation data along with Oreti River data has been collected by Environment Southland (D. May, personal communication, 20th August 2016). Queenstown, Roxburgh and Invercargill data has been collected by the Department of Chemistry, University of Otago (R. Frew, personal communication, 22nd August 2016).

Relationship between δ^2H and $\delta^{18}O$

The surface waters of the Waimea Stream plotted approximately on the global meteoric water line (GMWL) and showed moderate levels of fractionation (Figure 4-23). The Waimea Plains lie approximately 70km inland from the south coast of New Zealand and are separated from it by the

Hokonui Hills (Figure 4-22). Therefore, the observed fractionation is likely to be a result of the slight enrichment in ^{1}H and ^{16}O of precipitation falling on the Waimea Plains relative to coastal precipitation, due to the raining out of ^{2}H and ^{18}O containing water molecules as cloud masses move inland and to a greater elevation. The surface waters of the Waimea Plains plotted on the GMWL between, and were significantly different from (Figure 4-23) (p-value < 0.05), the coastal precipitation of Invercargill and Riverton, and the much more ^{2}H and ^{18}O depleted precipitation of inland Roxburgh and Queenstown (p-value < 0.05) (Figure 4-23). The surface waters of the Waimea Plains fell on the GMWL in approximately the same position as local precipitation on the Waimea Plains at Balfour. There was significant difference between the surface waters of the Waimea catchment and the Oreti River at Thee Kings and at Lumsden (p-value < 0.05).

This suggests that local precipitation falling within the Waimea catchment was most likely the predominant source of water across the Waimea Plains. The groundwater sample from bore E44/0036 had approximately the same isotopic composition as precipitation at Balfour, suggesting that the Waimea Plains groundwater is also principally sourced from rainfall falling locally. There was no evidence of any contribution of water from the Oreti River to the Waimea Plains surface water or groundwater.

Both February and March surface water samples showed evidence of high levels of surface water evaporation occurring to water within the Waimea and Longridge Streams. This was apparent in the significant shift towards less negative $\delta^{2}H$ and $\delta^{18}O$ values (p-value < 0.05) compared to April to July surface water, coupled with a shift towards a lower deuterium excess (p-value < 0.05). The February and March surface water samples were enriched in ^{2}H and ^{18}O in comparison to the April, May, June and July samples (p-value < 0.05). February and March also fell slightly off of the GMWL towards a greater proportion of oxygen-18, and thus have a reduced deuterium excess. This is characteristic of high levels of surface water evaporation occurring during the hotter months of February and March (Figure 4-23a) (Kendall & McDonnell, 1998).

The key findings from δ2H Vs δ18O were:

- Waimea Stream surface water had the same isotopic composition as local rainfall
- Waimea Stream surface water was significantly different from the Oreti River (p-value < 0.05)
- Waimea plains groundwater had the same isotopic composition as local rainfall (Balfour) and local surface water (Waimea and Longridge Streams).
- There was significant evaporation occurring to surface waters during February and March (P-value < 0.05).

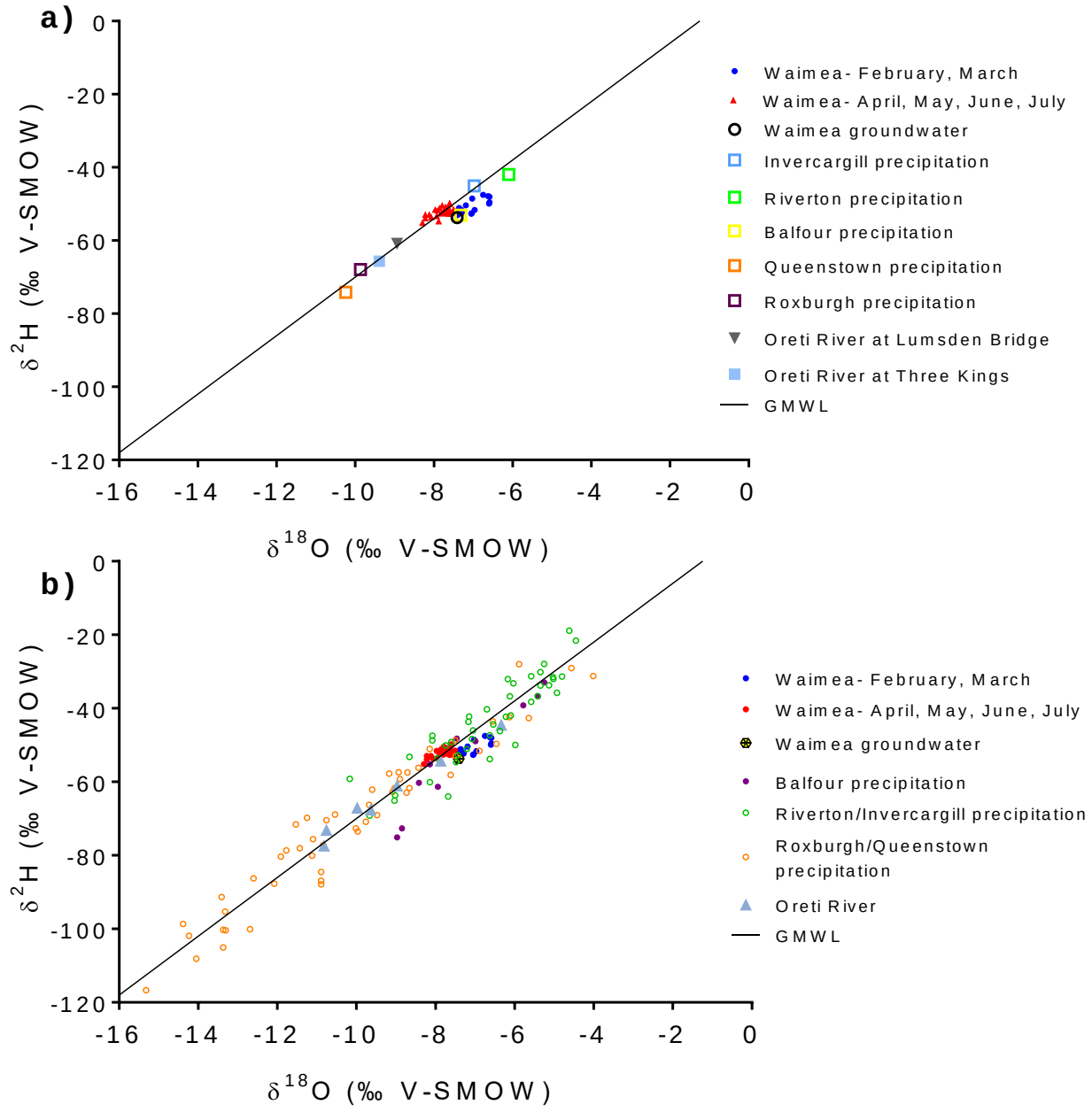

Figure 4-23 Waimea Stream surface water δ2H Vs δ18O. Water samples were collected monthly from the Waimea Stream (W-1 to W-8) (for map see Figure 2-1) for six months and were analysed for the stable isotope composition of hydrogen and oxygen using ICP mass spectrometry. δ^2H Vs delta $\delta^{18}O$ is plotted for a) Waimea Stream, with average precipitation and Oreti River data plotted and for the b) Waimea Stream, with all precipitation and Oreti River data plotted, relative to the global meteoric water line (GMWL). One groundwater sample (bore E44/0036) was taken during February. The isotopic composition of the Oreti River is at Three Kings and Lumsden Bridge. The precipitation data is for Invercargill, Riverton, Balfour, Queenstown and Roxburgh (for locations see Figure 4-22).

Spatial and temporal variation in deuterium excess and $\delta^{18}O$

During February and March surface waters exhibited a higher $\delta^{18}O$ (Figure 4-24b). This was interpreted as a result of evaporation of surface waters of the Waimea Catchment. An increased ^{18}O composition is particularly pronounced in the upper Waimea catchment at W-1 to W-3. However, at W-4 during both March and February there was a significant drop in $\delta^{18}O$, from approximately -6.6‰ at W-3, to -7.5‰ at W-4. The $\delta^{18}O$ for February and March at W-2 and W-3 was significantly less negative than at W-4 to W-7 (p-value < 0.05) (Figure 4-24a).

This drop in $\delta^{18}O$ at W-4 suggests at near this point in the Waimea Stream there was a large input of water that has not been exposed to the evaporation experienced in the upper Waimea Stream (W-1 to W-3). This may be the effect of a large input of groundwater over the 2 km between W-3 and W-4. Groundwater is not subject to evaporation occurring before it enters the Waimea Stream, hence once it does enter the stream, it will shift the isotopic composition of the surface water it contributed to. Further evidence of a groundwater input between W-3 and W-4 was that the $\delta^{18}O$ at W-4, and the groundwater sample from bore E44/0036 were both approximately -7.4‰ , whereas the $\delta^{18}O$ at W-2 during February and March was between -6.8 and -6.6‰ (Figure 4-24b).

Both February and March had significantly lower deuterium excess values, reflecting the greater levels of evaporation occurring during these two months (p-value < 0.05) (Figure 4-24a). From W-3 to W-4 there the deuterium excess value increased during both February and March towards a more positive deuterium excess at W-4. This may be the result of an input of water that has been subject to significantly less evaporation to the Waimea Stream near W-4, as less evaporated water will have a more positive deuterium excess, such as groundwater. During the wetter two months of May and July the deuterium excess across all sites on the Waimea Stream was approximately 10 (deuterium excess of the GMWL) suggesting that during these two months there was very little evaporation occurring to surface waters.

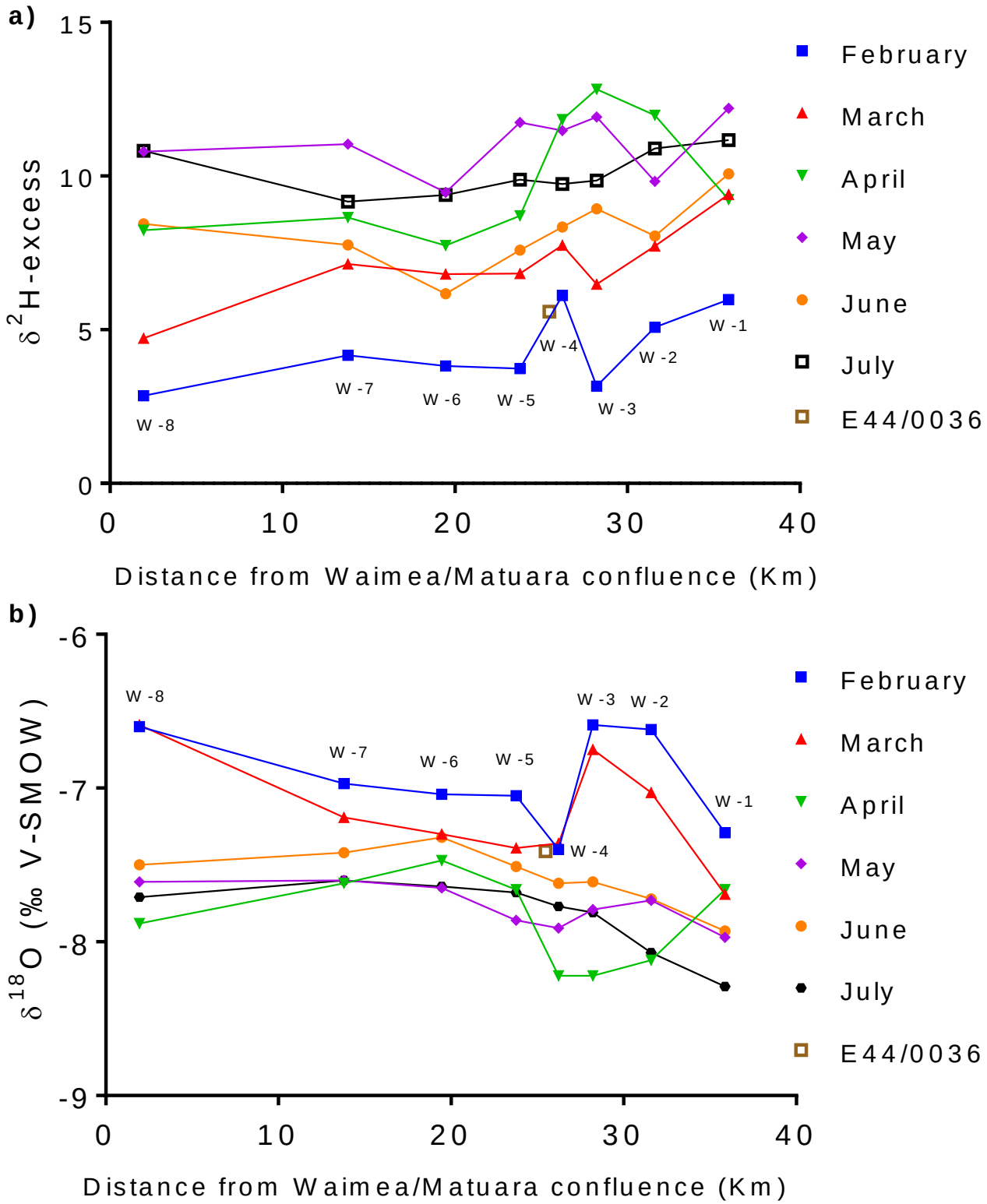

Figure 4-24 Waimea stream spatial isotopic composition. Water samples were collected monthly from the Waimea Stream (W-1 to W-8) (for map see Figure 2-1) for six months and were analysed for the stable isotope composition of hydrogen and oxygen using ICP mass spectrometry. One groundwater sample (bore E44/0036) was taken during February. The a) deuterium excess and b) $\delta^{18}O$ is plotted against the distance of the sampling site from the Waimea/Mataura confluence.

Relationship of Waimea Stream deuterium excess Vs ion ratios

In this section the ion ratios of Na:Cl and SO_4:Cl have been plotted against deuterium excess as a measure of evaporation. Particular focus has been given to February and March in comparison to July. This has been done to establish the hydrochemistry of the Waimea Stream during low flow, hot dry summer conditions and high flow, cold and wet winter conditions. These ratios have been plotted against deuterium excess so as to give an indication of whether the respective shifts in ion ratios were a result of evaporation. These ratios have also been compared to the ratio present in marine aerosols.

During February and March the Na:Cl ratio increased between W-2, which plotted closer to the Na:Cl of seawater, to W-3 to W-8, which exhibited a Na:Cl ratios between approximately 0.7-0.9 (Figure 4-25a). This compares to July which had a Na:Cl ratio range from 0.55-0.6 at W-2 to W-8. ANOVA analysis indicated that the differences in Na:Cl ratios between February/March and July was statistically significant (p-value < 0.05) (Figure 4-25a). Within each month there was no trend between an elevated Na:Cl ratio and deuterium-excess, indicating that the downstream between W-2 and W-3-8 in Na:Cl ratio was not the result of evaporation. However, between months, there was a significant correlation between a more negative deuterium excess, and a higher Na:Cl ratio (R^2=0.58). This is likely to reflect that during hotter and dryer conditions, groundwater with a high Na:Cl ratio, makes up a greater proportion of in-stream flow. The largely hill-fed site at W-1 had the greatest Na:Cl ratio of any site during both February and March as well as during July. The catchment of W-1 is steep hill country, with thin highly weathered soils overlaying bedrock (Rissmann et al., 2016a). This thin regolith combined with steep topography may explain the higher Na:Cl ratio at W-1 as water may interact with and weather rock material more readily.

Surface water during July in the Waimea catchment from W-2 to W-8 approximated the Na:Cl ratio of marine aerosols and had a deuterium excess of approximately +10. A Na:Cl ratio similar to precipitation suggests that during high flow events the water making up the in-stream flow has had little interaction with the local geological material, that would otherwise contribute Na and hence shift the Na:Cl ratio. During May to July the SO_4:Cl ratio was significantly greater than that of precipitation, ranging from approximately 0.7-1.0, compared to a precipitation ratio of 0.14. There was a significant positive relationship SO_4:Cl deuterium excess (R^2=0.6), for February to March. This may reflect that, as the level of evaporation decreases (indicated by a more positive deuterium excess), there is more excess water in the soil zone which flowing laterally and contributing higher levels of SO_4 to the Waimea Stream (Figure 4-25a,b).

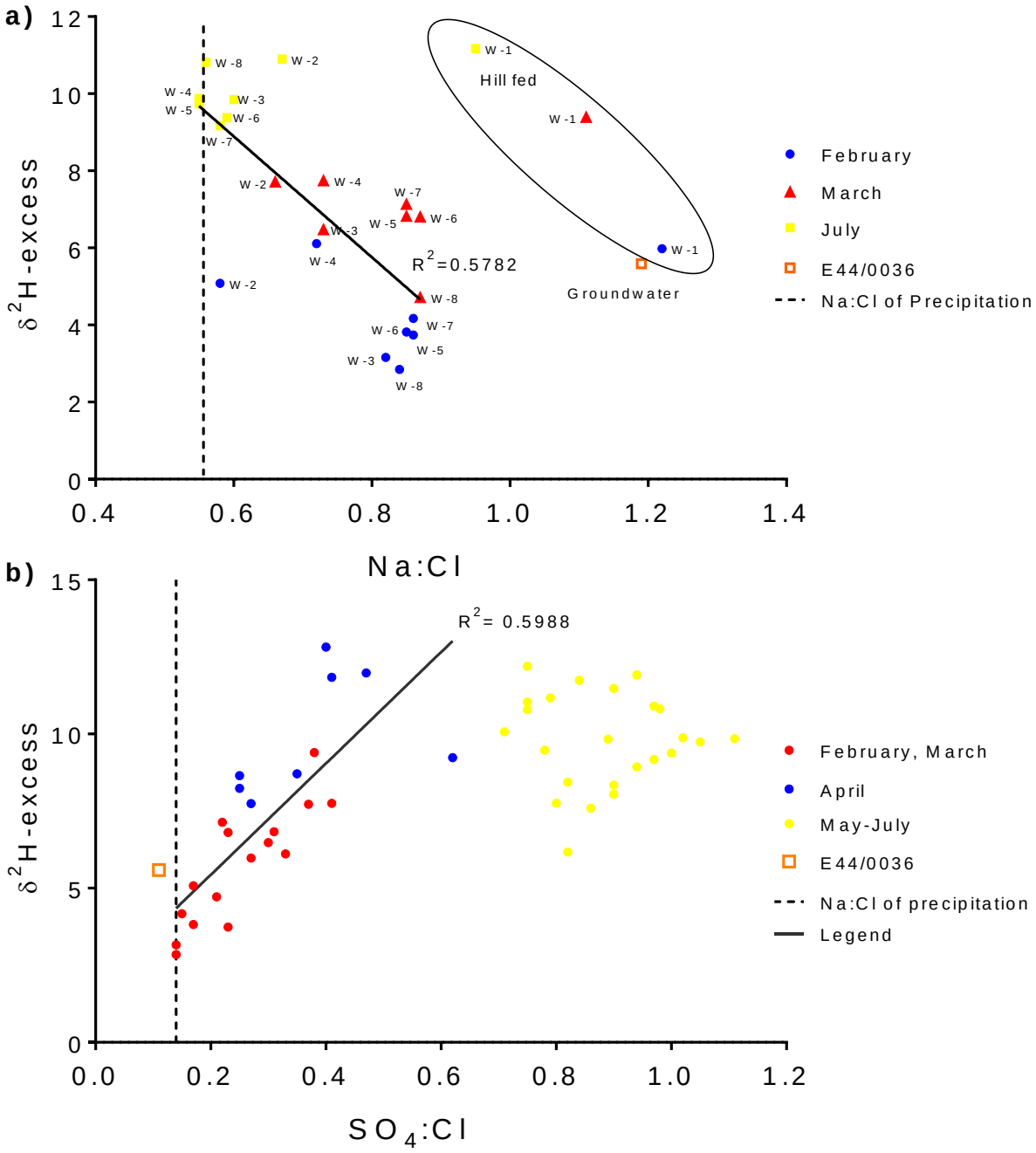

Figure 4-25 Waimea stream deuterium excess and ion ratios relative to the ionic composition of marine aerosols. Water samples were collected monthly from the Waimea Stream (W-1 to W-8) (for map see Figure 2-1) for six months and were analysed for the stable isotope composition of hydrogen and oxygen using ICP mass spectrometry. One groundwater sample (bore E44/0036) was taken during February. Here deuterium excess is plotted against a) the sodium:chloride ratio and b) the sulphate:chloride ratio for February to March and April to July. The respective ion ratio of seawater/marine aerosols is displayed.

4.5.2. Carbon stable isotopes

The stable isotope composition of carbon was investigated both spatially and temporally for the Waimea Stream. The composition of atmospheric carbon is approximately -8‰, while the composition of photosynthetically produced organic matter is approximately -27‰, which accumulates in the soil zone, and is consumed by microbes, resulting in a significantly lower $\delta^{13}C$ of DIC in the soil zone, and hence in groundwater.

The groundwater sample analysed had a much more negative $\delta^{13}C$ than any of the surface water samples taken, with a $\delta^{13}C$ value of -25.5‰ (Figure 4-26). The most negative surface water sample had a $\delta^{13}C$ of -18.4‰. The much more negative groundwater value will reflect the extensive interaction with the water entering the saturated zone and the isotopically fractionated DIC of the soil (Kendall & McDonnell, 1998). That the groundwater sample had a $\delta^{13}C$ that approximates that of the soil zone suggests that it has had very little DIC input from carbonate weathering (calcite $\delta^{13}C$= 0‰). Carbonate weathering otherwise acts to increase the $\delta^{13}C$ of groundwater. Groundwater contributions to surface water flow on the Waimea Plains can likely be identified by the input of a negative $\delta^{13}C$ groundwater isotopic composition.

Between W-1 and W-2 to W-4 and W-5 $\delta^{13}C$ declined by an average of -2.4‰ across all months monitored (Figure 4-26). This shift towards a lower $\delta^{13}C$ between W-1-2 and W-3-4 was significant, from a median of -13.6‰ at the former sites, to a median of -16.1‰ at the latter two sites (p-value < 0.05) Figure 4-27). This suggests a significant contribution of groundwater to flow around W-4 and W-5 on the Waimea Stream.

July had more negative $\delta^{13}C$ values compared to the previous five months (Figure 4-26). One way to interpret this could be that there was a greater contribution of groundwater during July than during the previous five months. This could result from a higher water table during winter (Rozenmeijer, 2007), or an increase in pressure as large quantities of water infiltrate through the vadose zone, thus increasing groundwater inputs to surface water bodies. An alternative interpretation is that during very wet high flow periods such as July, significant amounts of bank storage, as well as lateral flow through the unsaturated soil zone leads to an enhanced soil zone $\delta^{13}C$ composition in-stream, without necessarily an increase in groundwater contribution to in-stream flow. Bank storage is where during high flows the unsaturated soil zone either side of the stream become temporarily saturated, and then slowly releases water back into the stream as stream levels return to normal. Bank storage as well lateral flow through the soil zone is relatively short term, and thus does not impart the same kind of chemical composition of the groundwater end-member identified in the surface water hydrochemistry sections of this study.

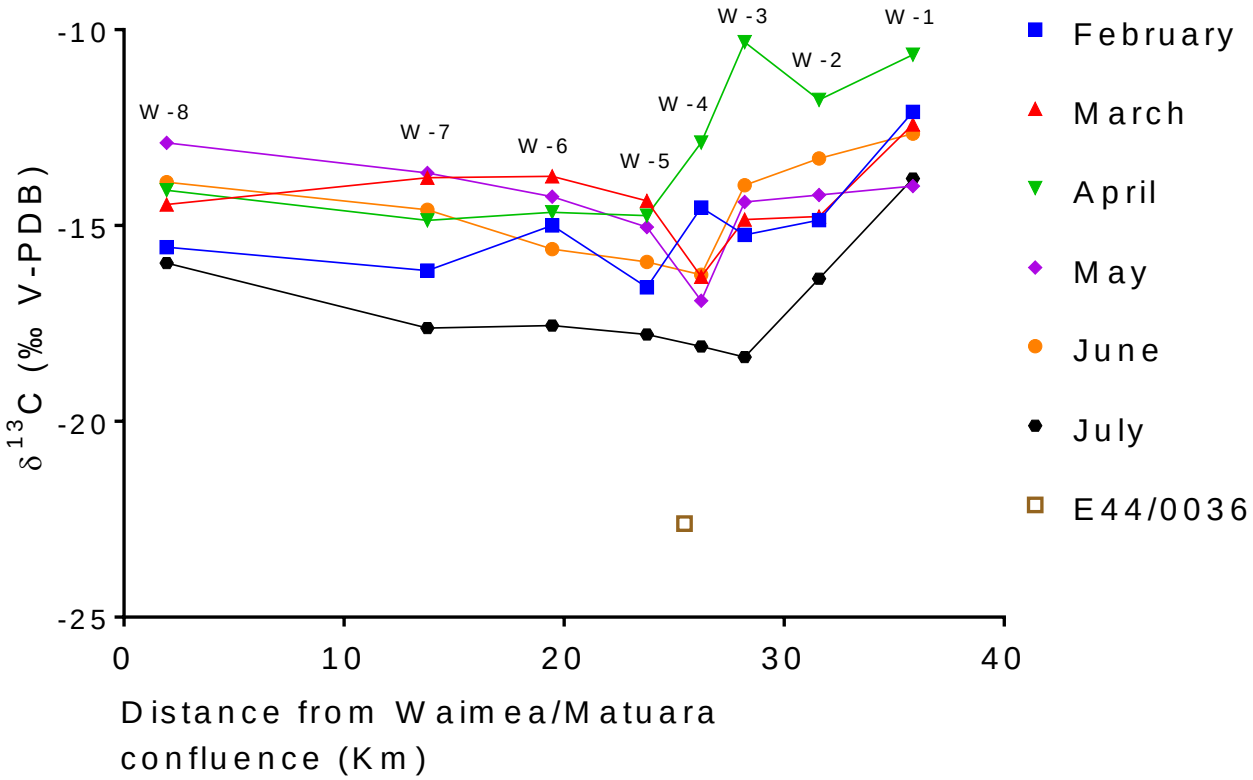

Figure 4-26 Waimea stream $\delta^{13}C$ spatial and seasonal variation. Water samples were collected monthly from the Waimea Stream (W-1 to W-8) (for map see Figure 2-1) for six months and were analysed for the stable isotopic composition of carbon using ICP mass spectrometry. One groundwater sample (bore E44/0036) was taken during February. Here $\delta^{13}C$ is plotted against the distance of the sampling site from the Waimea/Mataura confluence.

From W-1 to W-2 and W-4 to W-5 $\delta^{13}C$ decreased from a median of -13.6‰ at the former sites, to a median of -16.1‰ at the latter two sites (p-value< 0.05) (see 7). This suggests a significant contribution of groundwater to flow around W-4 and W-5 on the Waimea Stream.

From the mid-Waimea (W-4 & W-5) through to the lower Waimea (W-7 & W-8), $\delta^{13}C$ did not significantly change during February and April (Figure 4-27). However, during March, May, June and July the $\delta^{13}C$ at W-7 and W-8 was significantly higher than at W-4 and W-5, with the former having a median $\delta^{13}C$ of -14.2‰, and the latter a median $\delta^{13}C$ of -16.3‰ (p-value < 0.05) (Figure 4-27). This is likely to be the result of DIC outgassing in the lower Waimea Stream between W-5 and W-8. During this process ^{12}C-DIC species are preferentially released into the atmosphere, thus resulting in an enriched ^{13}C of the remaining surface water body (Kendall & McDonnell, 1998; Taylor & Fox, 1996). This occurs where there is little or no significant contribution of isotopically light groundwater, which would otherwise counteract DIC outgassing and maintain a low $\delta^{13}C$. This indicates that the principal contribution of groundwater occurs near W-4 and W-5 on the Waimea Stream, while from W-6 to W-8 there is little significant groundwater contribution to surface flow.

An alternate interpretation of the difference between the mid and lower Waimea is that photosynthetic aquatic plants are preferentially uptaking ^{13}C over ^{12}C, resulting in an enriched ^{13}C of the remaining surface water (Kendall & McDonnell, 1998). Significant levels of periphyton and macrophytes were observed in the Waimea Stream, especially in the lower reaches (W-3 to W-8). However, the shift in $\delta^{13}C$ occurred during May, June and July when photosynthetic levels would be greatly reduced due to colder conditions and less sunlight. Macrophyte and periphyton levels were also observed to drop considerably towards the winter months. This suggests that degassing in the lower reaches is a more likely explanation for the cause of this increase in $\delta^{13}C$ between W-4-5 and W-7-8.

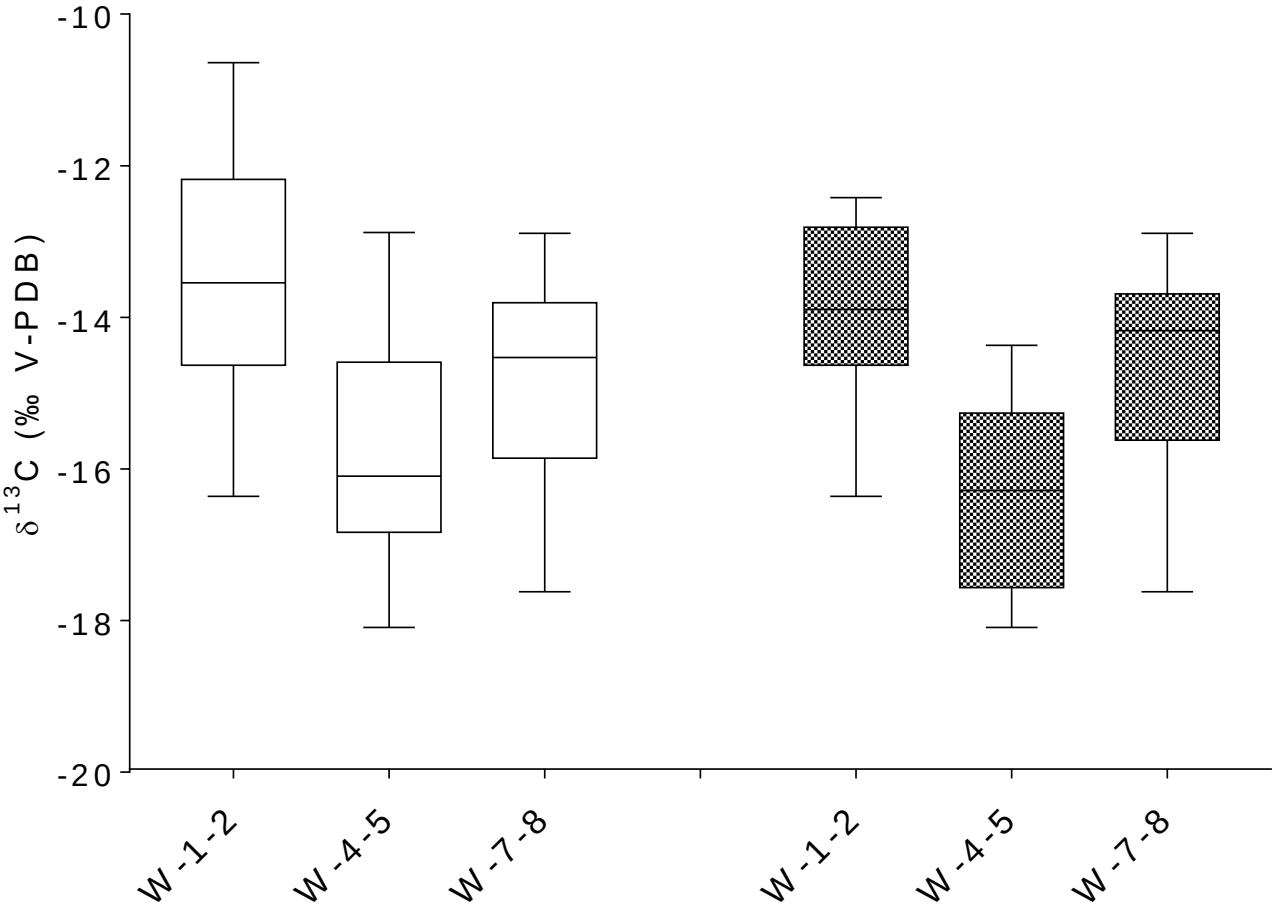

Figure 4-27 Waimea stream $\delta^{13}C$ in the upper, middle and lower reaches. Water samples were collected monthly from the Waimea Stream (W-1 to W-8) (for map see Figure 2-1) for six months and were analysed for the stable isotope composition of carbon using ICP mass spectrometry. Data collected is displayed for the upper Waimea (W-1, W-2), middle Waimea (W-4,W-5) and lower Waimea (W-7, W-8). Non shaded plots include data collected from February to July. There is a significant difference between W-1-2 and W-4-5 (p-value < 0.05). Shaded plots include data collected during March, May, June and July with a significant difference between W-1-2 and W-4-5, as well as between W-4-5 and W-7-8 (p-value < 0.05). Tukey plots with median and interquartile ranges a shown. Whiskers are 1.5X the interquartile range, red crosses are outliers.

4.6. Summary

4.6.1. Hydrochemistry

Spatial variation in chemistry

There was a large increase in Cl, Na, K, SO_4, Ca, HCO_3 and B between the upper Waimea Stream, and mid to lower Waimea Stream. Dissolved Mn was found to be elevated in the headwaters of the Waimea and Longridge Streams, while Fe was elevated in the headwaters of Longridge Stream.

Seasonal variation in chemistry

Summer surface water was found to be characterised by:

- HCO_3 dominance of major ion chemistry
- Elevated HCO_3, Na, and Mg.
- Elevated Mn and Fe in the headwaters
- Elevated Na:Cl ratio

Winter surface water was found to be characterised by:

- HCO_3 dominance in the headwaters, and Ca dominance in mid to lower reaches, of the major ion chemistry
- Elevated SO_4, K, Al and B
- Elevated SO_4: Cl ratio

4.6.2. Nutrients

Summer nitrate concentrations were:

- Low in the upper Waimea and Longridge Streams.
- Elevated in the lower Waimea and Longridge Streams.

Winter nitrate concentrations were:

- Elevated in the upper and lower Waimea Stream.

DRP concentrations were:

- Elevated throughout the Waimea Stream over winter during high flows.
- DRP concentrations were similar between summer and winter in Longridge Stream, with concentrations similar to the Waimea Stream during winter.

4.6.3. Sediment

There was a significant increase in sediment Ca, Mg, Mn, Cu, Co, Ni and Va over approximately 4 kms, in the mid-Waimea Stream (between W-5 and W-6). There was also a significant spike in sediment of Sb, K, Zn, Mb, B and Nb in the mid to upper Waimea Stream (at W-3).

4.6.4. Stable isotopes

Surface water of the Waimea stream was isotopically similar to local rainfall, and was significantly different from both coastal rainfall, and rainfall from further inland. The isotopic composition of the Waimea Stream surface water was also significantly different from the Oreti River.

There was evidence of high levels of surface water evaporation in the upper Waimea Stream over summer. There was a loss of this evaporation isotopic composition in the mid Waimea Stream, indicating a large input of groundwater.

In the mid Waimea Stream there was a shift in $\delta^{13}C$ that is indicative of a groundwater input to the Waimea Stream. In the lower Waimea Stream $\delta^{13}C$ suggested DIC outgassing, reflecting a lower level of groundwater connectivity.

On the Waimea Stream there was no trend between elevated Na:Cl ratios, and increased evaporation within a particular month. There was however between months (February, March and July excluding W-1). There was a trend during February to April between less evaporation as indicated by a higher deuterium excess, and an elevated SO_4:Cl ratio.

4.7. Integration of findings

In this section the key finding of Chapter 3 and 4 were integrated.

Hydrochemistry

The key hypotheses regarding summer and winter surface water chemistry reached in chapter 3 have been confirmed in chapter 4.

Two key differences in chemistry between chapter 3 and 4 were observed. Firstly, there was no significant winter increase in Ca concentrations in the Waimea Stream during 2016. Secondly, Mg was not found to seasonally alter significantly in Chapter 3, however, in chapter 4 it was found to decline significantly during winter.

In chapter 3 and 4, Na, K, SO_4 and HCO_3 were found to exhibit similar trends between summer and winter. Therefore, these four major ions have been used to characterise overland and groundwater end-members. Boron and aluminium were found to exhibit a significant difference between summer and winter and so have been also utilised to characterise winter in-stream chemistry.

From this the following characterisations of hydrological end-members has been established:

Overland flow was characterised by:

- Elevated SO_4 and a high SO_4: ratio.
- Elevated K
- Lower Na and HCO_3 concentration.
- Lower Na:Cl ratio (approaching the marine aerosol ratio of 0.55).
- Relatively high in-stream flow
- Elevated Al and B

Groundwater was characterised by:

- Higher Na and HCO_3 concentrations
- Lower SO_4, and a low SO_4:Cl ratio.
- Lower K, Al and B concentrations.
- Elevated Na:Cl ratio (median of 0.94)

Nutrients

During 2016, DRP was found to have similar spatial and temporal variation in concentration identified in Chapter 3. DRP was found to be highly elevated in the Waimea Stream during winter, while in Longridge Stream DRP concentrations were relatively high all year round relative to the Waimea Stream.

Two key findings confirmed in chapter 4 regarding nitrate were:

- Nitrate concentrations increased substantially in the middle reaches of the Waimea Stream (between W-3 and W-5).
- Nitrate concentrations in the upper Waimea Stream were elevated over winter, while in the lower Waimea Stream nitrate concentrations remained elevated during both summer and winter.

Chapter 5 Discussion

5.1. Overview of catchment surface water quality

The most significant variation in basic water quality parameters between sites was conductivity, which increased significantly between the headwaters of the Waimea Stream and the mid to lower reaches. The pH levels generally lay within the ANZECC guidelines for lowland (<150m) stream health, although pH outside of these trigger values at some sites in both the Waimea and Longridge Streams (Table 5-1).

Dissolved oxygen levels were generally in excess of 10 mg/L (or at approximately 100% saturation). However, in the headwaters of Longridge Stream, dissolved oxygen levels were as low as 2.2 mg/L. This falls well below the 98% saturation lower limit set by the ANZECC guidelines (ANZECCa, 2000). This is possibly the result of high levels of oxygen demand during high levels of plant matter decay and breakdown during summer (Allan et al., 2007). The headwaters of Longridge Stream had elevated Fe and Mn concentrations. These low oxygen levels may therefore be the result of an Mn and Fe rich seepage of anoxic groundwater (Freeze & Cherry, 1979). These reaches were very slow flowing and almost stagnant at the time these low oxygen readings were recorded. Slow flow may be contributing to lower dissolved oxygen concentrations as there is less water turbulence and hence aeration. Low oxygen levels can have an adverse effect on many aquatic organisms, and can also alter the redox state of the water, resulting in the release of previously bound nutrients and toxicants from the sediment (Allan et al., 2007; ANZECCb, 2000).

Turbidity was found to be highly elevated in the lower Waimea Stream, along with the headwaters of Longridge Stream (Table 5-1). This will be the result of the relative amounts of sediment input across these different reaches, which is likely to be a reflection of the relative intensity of land use, the level of riparian planting, and the degree to which stock are excluded from the waterway (Allan et al., 2007). These are all factors that will heavily influence the amount of bank erosion and sediment input into a stream. In regions that were naturally forested, such as New Zealand (Marie et al., 2015), the presence of riparian vegetation acts to stabilise stream banks, as well as filter sediment and nutrients (Gregory, Swanson, Mckee, & Cummins, 1991). Median turbidity values recorded in the lower Waimea Stream, along with the upper Longridge Stream, were above the ANZECC guideline value. During July, during very high in-stream flow, all sites within the Waimea Catchment had turbidity levels above the ANZECC guideline value (ANZECCa, 2000).

Only two sites within the Waimea Catchment had DRP concentrations close to, or below, the ANZECC guideline of 10µg/L for the prevention of nuisance macrophyte and periphyton growth. These were the two hill-fed sites, the headwaters of the Waimea Stream, and North Peak Stream, which drains the Hokonui Hills. All other sites had median DRP concentrations that exceeded this ANZECC guideline value. On a seasonal basis however, the upper Waimea Stream had a DRP concentration during summer 2016 of 12.1 µg/L, which is close to the guideline value. A major contributor to in-stream periphyton and macrophyte growth within the Waimea Catchment therefore is likely to also be high concentrations of DRP.

Nitrate concentrations during summer in the upper Waimea and upper Longridge Stream had nitrate concentrations that fell below the ANZECC guidelines (Table 5-1). The lower Waimea Stream and lower Longridge Stream over summer had nitrate concentrations consistently above the guideline nitrate concentrations. Through the winter months, all sites within the Waimea catchment had nitrate concentrations that exceed the ANZECC guideline for nitrate.

Excessive in-stream nitrate concentrations can also be directly toxic to aquatic species (Allan et al., 2007). Research has been undertaken in New Zealand on the toxicity of nitrate to both fish and macroinvertebrate species. For highly disturbed systems, for example catchments with intensive agriculture, in-stream nitrate concentrations need to be maintained below 2.4-3.6 mg/L in order ensure 80-90% protection of aquatic species (Hickey & Martin, 2011). Between 2006 and 2013, mean nitrate concentrations in the mid to lower Waimea Stream over winter (June to August), was consistently above 3.6 mg/L. During 2016, between May and July, nitrate concentrations in the mid to lower Waimea Stream were consistently above 3.3 mg/L, and as high as 6.6 mg/L. During February to July 2016, overall median nitrate concentrations in the mid to lower Waimea Stream was consistently above 4.3 mg/L, while in the lower Longridge Stream the median nitrate concentration recorded was 3.8 mg/L. Nitrate concentrations in the mid to lower Waimea Stream, and lower Longridge Stream, are therefore likely to be having a negative impact on fish and macroinvertebrate populations. This is supported by a recent survey of fish populations in the Waimea Stream that reported much lower fish numbers than were expected (Ledington, 2008).

Extensive periphyton and macrophyte growth was observed in the Waimea and Longridge Streams. This was particularly evident in the lower reaches of both streams. Periphyton and macrophyte levels were observed to decline dramatically over the winter months, despite significantly higher concentrations of in-stream nutrients that might otherwise promote growth. The flushing out effect during flooding events, coupled with reduced sunlight over winter may explain these lower levels of macrophyte and periphyton (Allan et al., 2007; Biggs et al., 1998). The flushing out of periphyton and macrophytes might produce feedback on in-stream nutrients by reducing the level of nutrient uptake by macrphytes and periphyton. This would then leave more nutrients remaining dissolved in the stream water.

Table 5-1 Summary of water quality parameters measured in the 2016 monitoring for this study, and ANZECC Guidelines for ecosystem health (95% protection level) (ANZECCa, 2000). Dashes indicate where there is no ecosystem protectionguideline given for New Zealand.

Parameter	Measured range	Median	Guideline value
pH	6.4-8.9	7.16	7.2-7.8
Turbidity (FAU)	<1-49	6	5.6
DO (mg/L)	2.16-14.18	10.61	98-105% saturation
Temperature (˚C)	4.8-24.5	9.45	-
Conductivity (µs/cm)	155.3-299	194.7	-
NO_3-N (mg/L)	<0.06-8.49	2.91	0.444
PO_4 (µg/L)	<10-157.6	24.05	10

5.2. Surface water Hydrochemistry

5.2.1. Spatial variation

Both Environment Southland's and the author's data was used to assess spatial and temporal variation in-stream chemistry.

There was a significant downstream increase in solute concentrations in the upper Waimea Stream (i.e between W-1 and W-4). Cl, SO_4, HCO_3, Na, K, Mg and Ca concentrations all increased substantially, along with conductivity, approximately doubling for many of these major ions. This spatial variation in chemistry is likely to be a combination of three key factors:

1. A relative depletion in the solute content of precipitation falling upon the Lintley Range (the catchment of the upper Waimea) relative to the Waimea Plains.
2. The difference in catchment topography and soil richness between upper and lower catchment, from relatively steep hill country to flat, rich, low lying plains.
3. The influence of groundwater on the mid to lower Waimea Stream.

Firstly, as rainfall moves inland and towards the centre of a land mass, the marine aerosol content tends to fall out, hence inland rainfall tends to have diminished aerosol content (Cook & Herczeg, 2000; Rossknecht, Elliot, & Ramsey, 1973). This factor results in a relatively reduced input of marine aerosols (Na, Cl, Mg, and Ca) to the catchment of W-1). For example, the average Cl content of precipitation falling on the Waimea Plains is 2.85 mg/L, which compares to an average of 0.75 mg/L on the Lintley Ranges (Rissmann et al., 2016b). North Peak Stream, the other hill-fed site monitored, had significantly higher Na and Cl concentrations compared to the headwater of the Waimea Stream. The catchment of North Peak Stream is closer to the coast than that of the Waimea Stream headwaters, and hence is likely to have rainfall with higher marine aerosol content. Thus, the elevated Na and Cl concentrations are likely to reflect the relative distance to the coast of the two catchments.

The ratio of the marine aerosols of Na and Cl across the catchment approximates the ratio found within marine aerosols indicating that Na and Cl are principally sourced from precipitation. There is, however, a slight shift away from the Na:Cl ratio of marine aerosols towards Na. This is most likely the result of water-rock interactions (Allan et al., 2007; Rissmann et al., 2016a). The marine aerosol ratios for surface waters within the Waimea catchment of Mg:Cl and Ca:Cl and SO_4:Cl are all elevated relative to that of marine aerosols. This suggests that there is a local contribution of Mg, Ca and SO_4 to in-stream chemistry, either from the soil zone, mineral weathering or anthropogenic inputs such as fertilizers (Allan et al., 2007).

Secondly, the shift in topography between the principally hill-fed catchment of W-1, to the where the Waimea Stream is predominantly lowland-fed at W-5, results in a large shift in the input of solutes derived from the much richer soil zone of the low lying Waimea Plains (Laing et al., 2008; Rissmann et al., 2016a). The catchment of W-1 consists of relatively steep terrain with a highly weathered soil zone, whereas the low lying Waimea Plains has a much younger, richer regolith (Rissmann et al., 2016a; Turnbull & Allibone, 2003). This richer regolith of the Waimea Plains will be contributing to the increase in in-stream solutes between W-1 and W-5. An additional factor is that the low lying Waimea Plains are subject to more intensive agricultural land use. A study in New Jersey Pinelands in the USA, found that streams draining watersheds that have been subject to intensive agricultural use had elevated Ca, Mg, K and SO_4 concentrations, which was postulated as relating directly from inputs from human activities (Morgan & Good, 1988).

Thirdly, Mg and Si were elevated at W-5 relative to upstream and downstream sites monitored on the Waimea Stream. W-5 corresponds approximately to where a previous study has found that there is a large gain in in-stream flow that could not be accounted for solely by flow inputs from the upstream catchment (K. Wilson, 2010). Groundwater is exposed silicate weather, thus, higher in-stream silica concentrations may be the result of large inputs of groundwater to the Waimea Stream near W-5. Silicate has been found in other studies to be a good tracer of groundwater (Inamdar, 2011; James & Roulet, 2006). Elevated Mg may also be the result of inputs to the Waimea Stream of water that has had more contact time with bedrock (i.e. groundwater) (Cook & Herczeg, 2000; James & Roulet, 2006). This is also reflected in the summer water facie at W-5, which is HCO_3-Mg-Ca, whereas at the up-stream and down-stream sites the water facie is HCO_3-Ca and HCO_3-Ca-Na type waters, respectively. Si correlates negatively with flow at W-5 and is thus elevated during low flows when groundwater is likely to dominate in-stream flow.

In the upper Waimea Stream there was a significant downstream increase in HCO_3 concentrations. This is interpreted as the influence of a greater contribution of groundwater rich in DIC to in-stream flow. Groundwater upwellings have been found to have significantly elevated HCO_3 concentrations (Gray, 2011; Jones & Mulholland, 1998; ÖQuist, Wallin, Seibert, Bishop, & Laudon, 2009). For example, partial pressures for DIC of 7-74 times that of the atmosphere have been observed in the Sleepers River watershed, Vermont, USA (Doctor et al., 2008).

Fe and Mn were generally found to be most elevated in the headwaters of the Waimea Catchment. This may reflect the influence of groundwater derived Mn and Fe on these headwater sites (Winter et al., 1998b). B increased markedly between the upper and mid Waimea Stream, and was also elevated in the upper Longridge Stream. This may reflect B rich soils of the gleyed physiographic unit present on the Waimea Plains contributing B to in-stream chemistry. B is present in clay rich soils such as the gleyed physiographic unit, and does not adsorb very strongly, and is thus readily released (Hounslow, 1995). The hill country catchment of W-1 consists of thin, highly weathered soils, and is thus likely to contain less B bound to clay.

5.2.2. Temporal variation

Seasonally, surface water pH was significantly lower during winter. This is likely to reflect a greater input of soil water to in-stream flow. The pH of soil water tends to be low due to the formation of acids from the decomposition of organic materials (McSween et al., 2003). This indicates that during winter there is likely to be an elevated direct input of soil water resulting from overland flow and lateral flow through the soil zone, which is probably assisted by the extensive artificial drainage (tile mole pipe) network that exists on the Waimea Plains. During July 2016, very high turbidity levels were recorded throughout the Waimea Catchment of an order of magnitude greater than the previous five months. This coincided with very high in-stream flows. Thus, the high turbidity is likely to be the result of large sediment inputs from farm runoff and bank erosion (Allan et al., 2007).

During April and March 2013 there was a large spike in Cl, HCO_3, Ca, Mg, Na, along with conductivity in the upper Waimea Stream (W-1 and W-3). This may be the result of solutes being flushed from the soil zone that have built up over a sustained dry period over summer (Piñol, Ávila, & rodá, 1992). High levels of evapotranspiration during summer can lead to the accumulation of solutes in soil water that is orders of magnitude greater than rainfall (Cook & Herczeg, 2000). This can build up, and then be subsequently flushed into waterways during wet periods after sustained dry periods.

The Longridge Stream at site L-3 recorded exceptionally high SO_4, Cl and K during April. For example, SO_4 was recorded as 30.3 mg/L, which compares to between 3.1 mg/L and 4.5 mg/L at the other sites monitored along Longridge Stream during April. A possible cause of this spike could have been a point source contamination of the fertilizer KCl along with a SO_4 containing fertilizer such as gypsum (Morgan & Good, 1988). These are commonly used fertilizers in New Zealand (Ravensdown, 2016).

During summer, HCO_3 and Na concentrations were elevated, which then dropped significantly over winter. During winter, SO_4, K, Al and B were elevated. Ca was found to be significantly elevated over winter in chapter 3, but a similar trend was not observed in chapter 4. These shifts in chemistry likely reflect a change in the dominant end-member contributing to in-stream flow between summer low flow conditions, and winter high flow conditions (Inamdar et al., 2013). Different end-members represent different pathways with which water makes its way to a stream. These different pathways confer a different chemical character on the water that entering the stream (Cook & Herczeg, 2000).

In-stream flow during summer is likely to be dominated by groundwater inputs which is characterised by an elevated Na:Cl ratio relative to marine aerosols, along with elevated HCO_3, Na and Mg concentrations. In a study of end-member inputs to a stream in the Piedmont region, USA, elevated Na was found to be a useful tracer of groundwater (Inamdar et al., 2013). An Na:Cl elevated ratio suggests a local source of Na resulting from water-rock weathering. Elevated in-stream Na:Cl is therefore likely to be the result of groundwater inputs to surface waters (Allan et al., 2007; Rissmann et al., 2016a). That this offset of Na:Cl from the SWDL towards Na is greatest over summer most likely reflects a greater proportion of groundwater contributing to surface water flow during the low flow conditions of summer.

HCO_3 and Na both correlated negatively with flow. A decrease in Na during high flow likely reflects the dilution of groundwater inputs of Na by significant inputs of overland flow with relatively low Na concentrations (Allan et al., 2007). This agrees with the shift to a Na:Cl ratio that approximates that of precipitation over the winter months, while during summer there is a shift toward higher Na:Cl ratio.

The HCO_3 decline observed during high flows may reflect two possibilities. Higher flows generally occur over winter when there is less photosynthesis occurring and the levels of DIC in the soil zone may be reduced as a result of lower inputs (less plant growth occurring) and the flushing of the soil zone that occurs during very wet conditions (Rightmire, 1978). This can result in soil water that enters the stream having less DIC. The drop in HCO_3 over winter may also be the result of reduced contributions of HCO_3 rich groundwater to in-stream flow during high flow winter conditions. Groundwater is often substantially enriched in DIC (Allan et al., 2007), thus a reduction in, or dilution of, groundwater inputs to surface water could result in reduced in-stream HCO_3 concentrations. A study in Sweden found that 90% of the variation of in-stream DIC could be accounted for by variation in groundwater inputs (ÖQuist et al., 2009).

During winter there was a significant increase in SO_4 and K. An elevated SO_4:Cl ratio suggests a local source of SO_4, for instance from the soil zone, which may be enhanced by the use of fertilizers such as pot ash or gypsum (Allan et al., 2007). A Na:Cl ratio of marine aerosols suggests that surface waters have not interacted significantly with local geological material (Allan et al., 2007), but rather in-stream water is derived from precipitation that has fallen relatively recently, and has quickly travelled via overland flow into the Waimea Stream. SO_4 has previously been found to be elevated after large rain events/wet periods, which was interpreted as the flushing out of the soil zone (Piñol et al., 1992). SO_4 is thus likely to be sourced from the soil zone during wet periods. Such lateral flow through the soil zone carries ions that are weakly bound to colloids into streams (Evans, 1989). A further factor that may be contributing to elevated SO_4 and K during winter is a reduction in demand due to lower levels of plants growth over winter. This would result in a larger excess of these solutes which is then flushed into waterways (Allan et al., 2007).

In 2016, B and Al were also found to be significantly elevated over winter. Both B and Al are likely to be sourced from the soil zone during wet periods of overland flow (Hounslow, 1995). For example, in the Piedmont region of the USA, Al was found to be a good tracer of surficial or overland flow (Inamdar et al., 2013).

5.3. Groundwater chemistry

Environment Southland data indicated that groundwater across the Waimea Plains consists of both HCO_3 and Cl dominated waters. The HCO_3 waters tend to occur up-gradient of the Balfour nitrate hotspot, while Cl dominated waters are located at, and down-gradient of, the Balfour nitrate hotspot. This is likely to reflect the relative age of the groundwater, with younger HCO_3 type groundwater

existing in the upper catchment, while further down the catchment, there is an evolution towards older Cl type waters (Freeze & Cherry, 1979). Greater groundwater Cl concentrations in the mid to lower Waimea Plains may also be the result of the influence of land use across the plains. There is evidence that the concentration of a number of major ions (SO_4 HCO_3 Cl, Na, Mg and Ca) is gradually increasing from two bores regularly sampled within the Balfour nitrate hotspot, E44/0036 and E44/0008. There was a correlation between elevated nitrate and elevated Cl, Na, Mg and Ca observed. This may reflect the influence of intensive land use impacting on the chemistry of groundwater on the Waimea Plains, and corroborates an earlier analysis of groundwater chemistry of the Waimea Plains (K. Wilson, 2010) which found a strong correlation between groundwater nitrate and Cl concentrations.

5.3.1. Distinctive ion ratios

Groundwater across the Waimea Plains had a median Na:Cl ratio of 0.94, which is significantly higher than that of marine aerosols (0.55) (Brezonik & Arnold, 2011). This is likely to be the influence of mineral weathering that groundwater is exposed to (Allan et al., 2007; James & Roulet, 2006). The enhanced Na:Cl ratio may thus be a useful tracer of groundwater inputs to surface waters. The SO_4:Cl ratio of groundwater across the Waimea Plains on the other hand had a median ratio of 0.12, which is slightly lower than that of marine aerosols (0.14) (Brezonik & Arnold, 2011). This suggests that there are no significant inputs of SO_4 to groundwater, additionally; it means that diminished in-stream SO_4 concentrations may indicate a high proportion of groundwater in surface waters.

5.3.2. Nutrient trends

Long term trends in groundwater nitrate concentrations within the Balfour nitrate hotspot indicate that nitrate concentrations have been steadily increasing over the past decade, increasing by approximately 0.3-0.5 mg/L per year. Nitrate concentrations within the Balfour nitrate hotspot range from approximately 10-25 mg/L, often exceeding the maximum allowable value for human drinking water of 11.3 mg/L (Ministry of Health, 2008). Nitrate concentrations from two bores in the upper Waimea Plains, outside of the Balfour nitrate hotspot, had nitrate concentration at or below 1.0 mg/L, with no apparent long term trend towards elevated nitrate concentrations. This difference is likely to reflect the different physiography these groundwaters are found under, in particular, the denitrification potential found within the unsaturated zone (Freeze & Cherry, 1979; Rissmann, 2012; Rissmann et al., 2016a). The Balfour nitrate hotspot coincides with the Old Mataura physiographic unit, which consists of highly weathered soils with low organic content and a low denitrification potential. The two bores with very low groundwater nitrate concentrations coincide with the gleyed physiographic unit, which has very high levels of denitrification potential (Rissmann et al., 2016a).

DRP concentrations from two bores within the nitrate hotspot have concentrations of approximately 15-25 µg/L. Bore E44/0008 indicated a slight trend towards lower DRP concentrations between 2000 and 2015, while E44/0036 did not exhibit any trend towards either higher or lower DRP concentrations.

5.4. Isotopic evidence

Stable isotope analysis has provided evidence that the surface water of the Waimea Plains is likely to be sourced principally from local precipitation falling on the Waimea Plains. Significantly different $\delta^{18}O$ and $\delta^{2}H$ compositions between surface waters and potential sources of water to a catchment, for example distal precipitation, is likely to indicate that these potential sources are unlikely to be contributing significantly to the catchments hydrology (Kendall & McDonnell, 1998). The isotopic composition of surface water of the Waimea Plains is not significantly different to that of local rainfall, while being significantly different from both coastal rainfall (at Riverton/Invercargill) and rainfall further inland (at

Queenstown/Roxburgh). Surface water also has a different isotopic composition from the Oreti River at the Lumdsden Bridge and at the Three Kings (for map see Figure 4-22). This suggests that there is little connectivity between the Oreti River and the Waimea Plains aquifer, despite the low level of relief between the two, despite the presence of an Otiran Oreti River flood channel across the Waimea Plains (Mcintosh et al., 1998).

The isotopic composition of Waimea Plains' groundwater is similar to local precipitation and surface water. This suggests that local groundwater is principally sourced from local rainfall. It also suggests that Waimea Plains' groundwater inputs to the Waimea Stream are not likely to alter substantially the isotopic composition of the receiving water.

Stable isotope analysis has also provided evidence that there is connectivity between the groundwater of the Waimea Plains and the Waimea Stream. It was found that this connectivity appears to principally exist in the middle reaches of the Waimea Stream around W-4 and W-5, with limited ground water connectivity in the lower Waimea (W-6 to W-8), possibly due to a confining bedrock layers in the lower reaches of the Waimea Stream. Two lines of evidence point towards this interpretation.

The $\delta^{18}O$ for February and March was significantly less negative in the upper Waimea compared to the mid to lower Waimea Stream. This is interpreted as the result of high levels of surface water evaporation occurring in the headwater of Waimea Stream resulting in an enhanced $\delta^{18}O$ composition (Kendall & McDonnell, 1998). This evaporative isotopic composition is then subsequently lost at W-4. This is likely to be due to a significant contribution of groundwater which is not subject to summer surface water evaporation, which acts to shift the isotopic composition of surface water away from the evaporative composition evident in the headwaters. This was also reflected in a spike in deuterium excess at W-4 during both February and March. A reduced deuterium excess is indicative of surface water evaporation occurring (Kendall & McDonnell, 1998). The spike to a higher deuterium excess at W-4 during February and March is therefore likely to be the result of groundwater contributing to in-stream flow, which acts to shoft the deuterium excess.

There was a significant drop in $\delta^{13}C$ in the mid reaches of the Waimea Stream. This is interpreted as resulting from an input of groundwater to in-stream flow which is imparting a significantly lower $\delta^{13}C$ to surface water. In the lower reaches of the Waimea Stream $\delta^{13}C$ was significantly elevated relative to the mid reaches. This is likely to result from DIC outgassing in the lower reaches of the Waimea Stream (Doctor et al., 2008), suggesting a much more limited level of groundwater connectivity in these lower reaches compared to the mid-reaches. A possible explanation for this is that confining layers of bedrock in the lower Waimea limit the level of connectivity between groundwater and the Waimea Stream, and thus limit the input of isotopically light DIC from groundwater (Kendall & McDonnell, 1998; Taylor & Fox, 1996).

At W-6, it was observed that the streambed was predominantly bedrock. In the upper Waimea, from W-2 through to W-4, the Waimea Stream runs across the middle of the Waimea Plains, which consist of fluvial deposits. However, from W-6 through to W-8 the Waimea Stream runs adjacent to the northern slopes of the Hokonui Hills. In this stretch of the river there is a patchwork of fluvial deposits as well siltstone and sandstones of the Dun-Mountain Matai terrane (Turnbull & Allibone, 2003). These siltstones and sandstones are possibly limiting the connectivity between groundwater and the Waimea stream between W-6 to W-8.

There is a significant increase in a suite of elements and trace elements in the sediment over only approximately 4 Km between W-5 and W-6. This may reflect the different geological materials that the stream is coming in contact with. Across the upper Waimea Stream the river runs across the middle of the Waimea Plains through slightly to heavily weathered quaternary fluvial deposits. It is around W-6

that the Waimea Stream, while running along the northern slopes of the Hokonui Hills, comes into close proximity to the siltstone and sandstones of the Dun- Mountain Matai terrane (Turnbull & Allibone, 2003). As the Waimea Stream moves from moderately to highly weathered quaternary fluvial deposits (Q2, Q4,Q6) to the relatively unweathered sandstone and siltstone, larger levels of metals, and trace metals are weathered and subsequently deposited within the sediment of the Waimea Stream.

The spike in antimony, potassium, zinc, molybdenum, boron and niobium could be the result of a groundwater input near this point which is bringing these elements to the surface in relatively significant amounts. W-3 is otherwise geologically in a large area of fluvial deposits, with the stretch of stream between W-2 and W-3 being highly weather quaternary deposits (Q6) (Turnbull & Allibone, 2003).

5.5. Major ion ratios and end-member chemistry

Summer low flows are thus characteristic of groundwater, while the winter high flows are characteristic of overland flow. Although average monthly rainfall levels do not vary greatly between summer and winter, the amount of evapotranspiration drops significantly over the winter months, approaching 0 mm, resulting in a large excess of surface water on paddocks during winter. This produces saturated conditions on the surface with significant amounts of overland flow occurring along with lateral flow through the soil zone into streams.

For the purposes of establishing groundwater inputs of nitrate to the Waimea stream, the chemical character of two principal end-members have been identified:

1. Lateral overland flow during wet periods which dominates the winter months.
2. Groundwater during dry periods which dominates the summer months.

The groundwater end-member which predominates during summer is characterised by:

- Lower in-stream flow
- Higher HCO_3, Na and Mg concentrations
- Lower SO_4 concentrations and a low SO_4: ratio.
- Lower K concentrations.
- Elevated Na:Cl ratio (median of 0.94)

The overland flow end-member which predominates during winter is characterised by:

- Higher in-stream flows
- Elevated SO_4 and a high SO_4: ratio.
- Elevated K, Al and B.
- Lower HCO_3, Mg and Na concentrations.
- Lower Na:Cl ratio (approaching the marine aerosol ratio of 0.55).

5.6. Implications for in-stream nutrient sources

5.6.1. Dissolved reactive phosphorus

There are two principal flow paths with which nutrients enter a stream, either via runoff/overland flow or through groundwater inputs (Allan et al., 2007). DRP inputs are generally confined to overland flow or runoff inputs as DRP tends to bind to or adsorb to colloids, meaning that it does not tend to travel readily down through the vadose zone and into the saturated zone. Nitrate on the other hand does not adsorb to colloids readily and thus can readily take a similar flow path to groundwater (assuming little denitrification occurring within the soil zone) (Freeze & Cherry, 1979).

In this study it was found that DRP was elevated in the Waimea Stream during winter, when runoff inputs were at their greatest. For example, when turbidity and flow was significantly elevated, DRP concentrations were also significantly elevated in the Waimea Stream. DRP in the Waimea Stream is thus likely to be principally sourced from overland flow. In 2016, it was found that during July, when sediment inputs to the Waimea Stream were strongly evident, DRP concentrations were at their greatest. This likely reflects the large input of DRP bound to sediment that enters the stream under high-flow conditions (Allan et al., 2007).

Longridge Stream exhibited quite a different dynamic in its upper reaches (L-1 to L-3) with DRP concentrations being high during summer low flow conditions and winter high flow conditions compared to the Waimea Stream. The downstream Longridge sitem, L-4 however, displayed a similar dynamic to the Waimea Stream, with relatively low DRP concentrations during summer, and relatively high concentration over winter.

5.6.2. Nitrate

The Waimea catchment can be divided into three different types of stream water in regards to nitrate dynamics:

1. Low nitrate (<0.5 mg/L) over summer, with a small increase over winter (remaining <1.5 mg/L)
2. Low nitrate (<0.5 mg/L) over summer, with elevated nitrate over winter (>2.0 mg/L)
3. High nitrate over summer (>1.5-2.0 mg/L), along with elevated winter nitrate (2.0-8.0 mg/L)

The first category was apparent in the upper Waimea Stream at W-1 and North Peak Stream (N-1). This is likely to reflect the relatively unintensive land use and poorer, more highly weathered soils, of the Lintley ranges which comprise the catchment of W-1, along with the Hokonui Hills, which comprise the catchment of N-1 (Ledgard, 2013; Rissmann et al., 2016a).

The second category is apparent in the upper Waimea (W-2 and W-3), Sandstone Stream (S-1) and the upper Longridge Stream. This is likely to reflect the relatively intensive landuse of the catchment of these sites in comparison to W-1 and N-1. The principal flow path of nitrate in the first and second categories is overland flow along with lateral flow through the soil zone. This is evidenced by the correlation of SO_4, with elevated nitrate across reaches where this nitrate dynamic is apparent, along with an inverse relationship with Na, which has been identified in the study as a signature of groundwater dominated low flow (i.e. higher Na correlates with lower nitrate concentrations).

The third category is similar to category two, but also has elevated nitrate concentrations over summer (in excess of 1.5-2.0 mg/L), and is apparent in the lower Waimea (W-4 to W-8) and Longridge stream (L-4). This corresponds to where groundwater connectivity has been identified in this study at W-4 and W-5. W-4 and W-5 are also geographically near the Balfour groundwater nitrate hotspot. Thus the groundwater of the Balfour nitrate hotspot is likely to be contributing significant levels of nitrate to the Waimea Stream between W-3 and W-5.

The elevated summer nitrate apparent in category three is likely the result of groundwater inputs to in-stream flow that is elevated in nitrate during low flow conditions. In the lower Waimea Stream (W-5, W-7 and W-8), nitrate concentrations do not correspond with SO_4 nor with Na. This suggests that nitrate has a source other than the soil zone/overland flow, as nitrate concentrations would otherwise decrease when SO_4 concentration decrease. There is also a significant input of overland flow derived nitrate in these lower reaches during high flows as nitrate concentrations do not drop when the proportion of groundwater making up flow declines (Na concentration decrease). When Na concentrations do decline, as overland flow input increase, there would otherwise be a dilution of in-stream groundwater derived nitrate.

Chapter 6 Conclusions

6.1. Key findings

The surface and groundwater of the Waimea Plains is likely to be principally sourced from precipitation falling locally. Water within the Waimea Stream and Waimea Plain's aquifer is thus very dependent on the level of local rainfall that occurs, with no recharge evident from outside of the Waimea catchment, such as seepage from the large, alpine-fed, Oreti River.

Overland flow has been found to dominate the flow of the Waimea Stream during the wetter winter months, while groundwater contributes significantly to flow during summer. The former is characterised by elevated in-stream concentrations of SO_4, K, Al, B, a Na:Cl ratio of marine aerosols and a substantially elevated SO_4:Cl ratio. The key characteristic of groundwater dominated flows was found to be elevated HCO_3, Na and Mg, along with an elevated Na:Cl ratio relative to marine aerosols.

Groundwater mainly contributes water to the Waimea Stream in the middle reaches near Balfour (W-4 and W-5). In the lower Waimea Stream there is evidence that there is less connectivity, possibly due to confining bedrock layers, where the Waimea Stream runs along the northern edge of the Hokonui Hills.

Nitrate concentrations throughout the Waimea catchment are elevated over winter, when the overland flow end-member dominates in-stream flow, and hence is likely to be a major pathway for nitrate entering the Waimea Stream. DRP is also significantly elevated throughout the Waimea Stream during winter, suggesting that overland flow is also the major source of in-stream DRP.

In summer only the mid to lower reaches the Waimea Stream have elevated nitrate concentrations, when the groundwater end-member dominates in-stream chemistry. Thus, in the mid to lower Waimea Stream during summer, groundwater, high in nitrate from the Balfour nitrate hotspot, is likely to be the source of elevated downstream nitrate.

6.2. Nutrient management implications

Management of the Waimea Stream in the first instance should focus on reducing the input of nutrients via the overland flow, or farm runoff pathway. It was observed that some reaches of the Waimea Stream have no fencing to exclude stock or any significant riparian planting. It was also observed that stretches of the Waimea Stream's banks were showing signs of high erosion rates. Ameliorating these inputs of nutrients can best be achieved through measures such as fencing off of waterways to exclude stock, and riparian planting to reduce and filter sediment input. Riparian planting would also be beneficial in terms of reducing bank erosion and by providing shading, which acts to limit periphyton and macrophyte growth. These steps, coupled with good management of nutrient budgets on farm, will help reduce the input of both nitrates and DRP to the Waimea Stream via farm run-off.

Nitrate inputs from groundwater are much harder to address and ameliorate. The first priority would need to be limiting further losses of nitrate from farm paddocks down into the groundwater system through good nutrient budgeting and farm management. One possible avenue to address high groundwater nitrate is managed aquifer recharge, whereby aquifer recharge is enhanced, resulting in a greater volume of water entering the aquifer, and hence the dilution of groundwater nitrate (Schmidt et al., 2001). Thus groundwater nitrate concentrations are reduced, resulting in lower inputs of groundwater derived nitrate to surface water. This, however, is likely to be a very costly solution.

The nuisance growth of periphyton and algae requires both available nitrate and DRP. The steps outlined above that reduce inputs of DRP to the Waimea Stream, should act to limit nuisance growth in the Waimea Stream, even if groundwater continues to contribute high levels of nitrate to the mid and lower Waimea Stream. Hence, focusing on limiting overland inputs of nutrients should alone be able to limit nuisance periphyton and macrophyte growth.

6.3. Limitations of this study

A limitation of this study was the frequency and spatial spread of sampling. This is principally due to constraints in both time and funding. The main method used in this study involved taking a discrete grab sample at a single point in time and space once a month. The limitation of this approach is that it is not able to capture finer levels of temporal and spatial variation that may, for example, be occurring on an hourly or daily basis. The data collected therefore may not be at a fine enough temporal resolution to capture significant hydrochemical variation that is occurring. For example, a certain parameter may fluctuate greatly, but at the point in time when all the samples collected for this study were taken this particular parameter was peaking. Thus, the data collected will not reflect the true load of this parameter, and will in fact greatly exaggerate the actual loading of this parameter. Probes that sit continuously in a stream and give real-time data, on for example, temperature or nitrate concentrations, can provide a very fine temporal resolution of data. Auto-samplers that just collect data during flooding events or very low flows would also be useful to overcome this limitation. However, these types of sampling are a very costly form of monitoring to set up.

During 2016, monitoring was only carried out for 6 months. A full year's worth of monitoring would have been useful in establishing differences in summer and winter in-stream chemistry and nutrient levels.

The spatial spread of data collection is the other chief limitation of this study, as data collection was carried out at discrete sites within the Waimea Catchment. This approach can only reflect the state of a stream at particular spatial points. Thus, exactly where significant shifts in hydrochemistry occur may not be accurately identified, or indeed completely missed. For example, a major groundwater input may occur between two sites, with a signature of this input being too faint to identify at the downstream site, and is thus missed entirely. This can be compensated for by using a greater number of sites, and thus enhancing the discrete spatial resolution. Another possible approach is to use probes that are laid along the length of a stream. This would enable the analysis a particular variable at the resolution of a metre or less.

Only one groundwater sample was able to be taken during this study. More groundwater samples providing a wider picture of groundwater chemistry would have been desirable. This was not possible due to the difficulty of accessing bores on private land and needing pumping equipment to access the groundwater. In particular, more groundwater samples giving a more comprehensive picture of groundwater isotopic composition would be useful in providing a more robust conclusion regarding inter-catchment transfer between the Oreti River and the Waimea Plains.

6.4. Recommendations for future research

This study used seasonal variation in in-stream chemistry along with an analysis of groundwater chemistry in order to establish two broad hydrological end-members within the Waimea catchment. These end-members could potentially be defined further into different types of overland flow, for

example, deep and shallow soil water, direct precipitation, riparian soil water, event or storm water, hill slope, and indeed different groundwater end-members, perched, shallow and deep groundwater (Inamdar, 2011). In order to establish the chemistry of these different end-members further research could be undertaken whereby samples of, for example, soil water, is sampled and analysed directly. The chemistry of these end-members, which have been established independently of in-stream chemistry, could then be compared to changes in in-stream chemistry during different flow conditions. From this it could then be establish with more precision which end-members contribute to in-stream flow, in what proportions, and under what conditions.

There is evidence of little connectivity between the Oreti River and the Waimea Plains ground and surface waters. Only one groundwater sample from the Waimea Plains aquifer was analysed for isotopic composition in this study. A wider sampling of groundwater across the Waimea Plains, with replicates, would be needed to provide a more robust answer to the question of any possible Oreti River connectivity with the Waimea Plains aquifer.

Extensive periphyton and macrophyte growth was observed in both the Waimea and Longridge Streams. Thus study has demonstrated that groundwater with high nitrate concentration is entering the middle reaches of the Waimea Stream which is resulting in highly elevated in-stream nitrate concentrations over summer in the mid to lower Waimea. Further study is needed in order to understand the affects this is having on the ecology of the Waimea Stream in terms of, for example, macrophyte and periphyton growth, benthic community health and fish population health. The Waimea Stream has anecdotally been considered to be a rich trout fishery, although evidence suggests that the fish population in the Waimea Stream is currently not very healthy (Ledington, 2008). Further research is thus required to understand the relationship between water quality and the ecological health of the Waimea Stream.

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Appendix

Appendix A: 2016 basic water quality and major ion data

Site No.	Coordinates	Date	pH	Oxygen	Temperature	Conductivity	Turbidity	Nitrate (NO_3-N)	DRP (PO_4)	Cl	SO_4	HCO_3	Na	Mg	K	Ca	Ion balance
	Lattitude, longitude			mg/L	C	µs/cm	FAU	mg/L	µg/L	mg/L	mg/L	mmol/L	mg/L	mg/L	mg/L	mg/L	(anions/cations)/total ions
W-1	-45.767164, 168.491821	14/02/2016	7.03	9.89	16.60	97.10	4.00	0.02	32.12	7.10	1.90	0.85	8.64	2.58	0.69	8.40	-3.96
W-2	-45.804153, 168.516197	15/02/2016	6.73	7.67	18.60	144.40	2.00	0.05	22.32	17.20	3.00	1.18	10.05	4.13	1.80	16.05	-9.13
W-3	-45.839803, 168.533192	15/02/2016	7.24	10.68	18.80	201.10	8.00	0.09	90.90	18.90	2.60	1.81	15.56	8.39	0.74	16.88	4.74
W-4	-45.876624, 168.528900	14/02/2016	7.08	10.25	24.50	221.00	9.00	4.75	22.32	22.00	7.20	1.25	15.84	9.77	0.61	15.38	-5.48
W-5	-45.898252, 168.549500	15/02/2016	6.86	10.25	17.50	222.00	4.00	2.21	32.12	21.00	4.80	1.60	17.97	9.14	0.63	15.70	2.71
W-6	-45.925483, 168.592243	14/02/2016	7.38	10.51	17.50	189.20	9.00	2.39	66.40	20.00	3.40	0.99	17.08	6.79	0.54	13.39	-8.16
W-7	-45.944943, 168.660393	15/02/2016	7.47	9.61	18.50	194.10	4.00	2.72	73.75	21.00	3.20	1.14	18.01	7.08	0.40	13.75	-5.29
W-8	-45.987301, 168.80064	14/02/2016	7.19	9.20	19.70	183.20	10.00	2.40	78.65	21.00	3.00	1.06	17.61	6.32	0.60	12.81	-4.95
L-1	-45.783686, 168.557053	14/02/2016	6.71	2.16	16.20	172.70	16.00	0.03	90.90	14.30	1.80	1.63	12.62	5.45	2.81	15.87	5.01
L-2	-45.803555, 168.595161	14/02/2016	7.03	4.68	18.30	299.00	8.00	0.00	166.82	12.10	4.50	2.43	15.68	11.30	0.47	25.19	-1.54
L-3	-45.838009, 168.596191	14/02/2016	6.83	8.15	19.50	173.00	13.00	0.07		13.40	0.60	1.61	12.05	6.48	1.32	15.20	-0.12
L-4	-45.886304, 168.601856	15/02/2016	6.85	11.89	16.20	152.30	5.00	1.10	66.40	16.90	2.10	0.84	14.67	4.24	0.47	11.21	-6.43
E44/0036	-45.867797, 168.550647	15/02/2016	6.75	10.34	12.50	2.90	0.00	5.69	27.22	16.50	1.80	1.03	19.58	5.68	1.04	12.33	-11.05
W-1	-45.767164, 168.491821	13/03/2016	7.42	10.37	12.00	95.00	0.20	0.01	41.91	7.48	2.88	0.59	8.31	2.56	0.68	6.27	2.61
W-2	-45.804153, 168.516197	12/03/2016	8.90	11.95	16.60	110.20	4.00	0.01	19.87	13.04	4.84	0.50	8.66	2.88	0.91	6.08	-1.28
W-3	-45.839803, 168.533192	13/03/2016	7.72	10.60	13.60	146.40	7.00	0.01	56.61	14.84	4.44	1.01	10.85	4.97	1.42	9.25	5.06
W-4	-45.876624, 168.528900	13/03/2016	7.74	13.43	13.80	227.00	0.20	3.16	71.30	20.56	8.41	1.01	14.96	9.53	0.92	11.52	-6.95
W-5	-45.898252, 168.549500	12/03/2016	8.39	12.59	14.70	221.00	3.00	3.88	34.56	20.06	6.17	0.88	17.00	8.59	0.95	11.39	-12.87
W-6	-45.925483, 168.592243	12/03/2016	8.69	13.52	13.20	201.50	5.00	3.35	46.81	19.60	4.53	0.90	17.14	6.96	0.86	10.15	-8.77
W-7	-45.944943, 168.660393	12/03/2016	8.38	12.57	12.80	200.00	7.00	2.55	56.61	20.11	4.44	0.90	17.02	6.72	0.83	10.15	-7.68
W-8	-45.987301, 168.80064	12/03/2016	7.17	10.11	12.40	197.70	4.00	1.77	49.26	20.79	4.30	0.99	18.06	6.60	1.00	10.49	-5.93
L-1	-45.783686, 168.557053	13/03/2016		9.81	11.90	160.40	13.00	0.17	208.45	13.50	3.52	1.35	11.59	4.79	3.10	9.78	10.43
L-2	-45.803555, 168.595161	13/03/2016	7.14	4.50	12.20	224.00	15.00	0.01	247.64	12.89	3.46	2.16	14.97	9.72	0.99	16.92	5.67
L-3	-45.838009, 168.596191	12/03/2016	8.83	14.88	16.30	178.20	4.00	0.02	262.34	13.59	2.66	1.26	12.89	6.90	0.94	12.14	-1.65
L-4	-45.886304, 168.601856	13/03/2016	7.17	9.27	15.40	153.60	4.00	1.14	103.14	17.16	2.31	0.83	14.85	3.92	0.50	8.40	-1.27
W-1	-45.767164, 168.491821	10/04/2016	7.61	11.14	12.60	83.00	0.00	0.01	14.97	6.37	3.93	0.52	7.16	2.07	0.66	5.23	-1.73
W-2	-45.804153, 168.516197	10/04/2016	7.14	10.96	9.70	98.50	5.00	0.02	22.32	9.20	4.30	0.58	7.90	2.82	0.93	6.09	-1.63
W-3	-45.839803, 168.533192	9/04/2016	8.00	11.54	12.70	106.50	8.00	0.01	66.40	10.47	4.14	0.62	8.42	3.27	1.11	6.51	0.62
W-4	-45.876624, 168.528900	9/04/2016	8.50	13.99	14.90	179.90	5.00	2.51	39.46	16.73	6.89	0.85	12.93	7.60	1.38	10.58	-8.94
W-5	-45.898252, 168.549500	9/04/2016	7.82	11.93	13.70	185.80	4.00	3.29	39.46	17.11	5.92	0.92	13.80	7.15	1.17	10.11	-6.04
W-6	-45.925483, 168.592243	9/04/2016	8.40	12.46	13.10	192.20	5.00	2.79	49.26	18.75	5.11	0.83	14.98	6.61	1.20	9.93	-7.88
W-7	-45.944943, 168.660393	9/04/2016	7.42	9.86	11.90	202.60	7.00	2.64	73.75	19.86	4.99	0.92	17.12	7.04	1.30	11.11	-9.27
W-8	-45.987301, 168.80064	9/04/2016	7.35	9.42	12.40	203.70	5.00	3.39	73.75	20.45	5.03	1.01	16.91	6.68	1.21	11.26	-5.31
L-1	-45.783686, 168.557053	10/04/2016	7.08	8.15	9.90	127.90	14.00	0.07	193.76	10.62	3.84	1.04	10.23	3.83	2.20	7.97	7.70
L-2	-45.803555, 168.595161	10/04/2016	7.11	2.26	10.20	245.00	10.00	0.12	208.45	16.80	4.50	1.94	14.49	9.58	4.24	17.22	2.39
L-3	-45.838009, 168.596191	9/04/2016	7.77	9.21	16.20	145.00	8.00	1.05		32.44	30.34	0.93	13.61	8.12	15.42	17.91	-1.42
L-4	-45.886304, 168.601856	9/04/2016	7.31	11.13	14.90	163.60	2.00	3.39	132.53	16.40	3.16	1.00	14.62	4.45	0.96	9.40	1.03

Site No.	Coordinates	Date	pH	Oxygen	Temperature	Conductivity	Turbidity	Nitrate (NO_3-N)	DRP (PO_4)	Cl	SO_4	HCO_3	Na	Mg	K	Ca	Ion balance
	Lattitude, longitude			mg/L	C	µs/cm	FAU	mg/L	µg/L	mg/L	mg/L	mmol/L	mg/L	mg/L	mg/L	mg/L	[anions/cations)/total ions
W-1	-45.767164, 168.491821	22/05/2016	7.29	10.94	8.20	95.00	6.00	0.57	37.01	8.25	6.16	0.53	7.74	2.39	0.91	6.30	-1.26
W-2	-45.804153, 168.516197	21/05/2016	7.11	10.57	8.70	135.20	5.00	3.12	44.36	15.52	13.77	0.48	8.68	3.44	1.09	8.82	-3.16
W-3	-45.839803, 168.533192	22/05/2016	7.34	10.47	8.40	166.20	8.00	3.03	86.00	19.11	17.88	0.50	10.14	4.53	1.63	11.13	0.07
W-4	-45.876624, 168.528900	22/05/2016	7.30	10.34	8.40	205.10	5.00	3.50	63.95	21.46	19.34	0.70	11.33	6.51	1.99	13.19	-0.85
W-5	-45.898252, 168.549500	21/05/2016	7.52	10.74	9.20	206.10	8.00	5.49	68.85	21.45	18.12	0.62	11.92	6.51	2.05	13.42	-5.07
W-6	-45.925483, 168.592243	21/05/2016	7.65	11.29	8.90	208.70	6.00	4.66	63.95	21.58	16.77	0.61	12.57	6.17	2.02	13.80	-6.61
W-7	-45.944943, 168.660393	21/05/2016	7.60	11.10	8.70	206.40	5.00	4.82	59.06	21.94	16.56	0.59	12.90	6.12	2.07	13.56	-7.24
W-8	-45.987301, 168.80064	21/05/2016	7.50	10.83	8.20	207.50	14.00	6.60	56.61	22.73	17.04	0.56	12.62	5.77	2.14	13.48	-5.80
L-1	-45.783686, 168.557053	22/05/2016	7.15	10.50	8.30	160.60	8.00	4.10	34.56	13.57	14.51	0.56	10.21	4.28	1.71	10.40	-4.48
L-2	-45.803555, 168.595161	22/05/2016	7.15	8.91	8.40	232.00	3.00	4.49	68.85	19.19	20.97	0.90	12.72	7.91	2.04	17.54	-6.24
L-3	-45.838009, 168.596191	21/05/2016	7.31	10.88	9.10	230.00	6.00	8.49	63.95	20.41	21.03	0.56	12.33	6.53	2.14	16.71	-10.94
L-4	-45.886304, 168.601856	21/05/2016	7.38	10.62	9.20	219.70	4.00	6.60	115.39	19.50	15.73	0.62	12.76	5.97	2.00	15.35	-10.88
W-1	-45.767164, 168.491821	13/06/2016	7.08	11.49	7.50	104.50	3.00	0.29	48.63	9.28	6.56	0.55	8.24	2.45	0.74	6.45	-2.75
W-2	-45.804153, 168.516197	13/06/2016	6.85	12.08	4.80	161.50	3.00	1.71	43.75	12.32	11.13	0.56	9.72	4.58	1.26	10.95	9.62
W-3	-45.839803, 168.533192	13/06/2016	7.11	11.56	7.60	193.70	5.00	1.39	55.95	15.49	14.57	0.63	11.27	5.68	1.73	13.52	-9.93
W-4	-45.876624, 168.528900	13/06/2016	7.13	11.35	8.30	231.00	6.00	3.55	153.51	18.46	16.54	0.82	12.69	8.52	2.00	14.89	-9.67
W-5	-45.898252, 168.549500	13/06/2016	7.18	11.44	8.40	227.00	6.00	3.88	104.73	18.90	16.28	0.81	13.74	8.49	1.88	14.90	-10.85
W-6	-45.925483, 168.592243	13/06/2016	7.36	13.39	6.80	222.00	3.00	3.86	107.17	19.35	15.80	0.81	13.65	7.33	1.77	14.11	-7.27
W-7	-45.944943, 168.660393	13/06/2016	7.29	12.06	6.10	219.70	6.00	3.28	97.41	19.43	15.59	0.79	13.92	7.25	1.81	14.28	-8.25
W-8	-45.987301, 168.80064	13/06/2016	7.32	12.06	7.20	224.00	7.00	4.03	116.92	19.94	16.40	0.78	14.39	6.91	1.80	14.31	-7.49
L-1	-45.783686, 168.557053	13/06/2016	6.93	10.56	9.10	161.20	13.00	1.41	55.95	13.73	14.58	0.67	10.69	4.57	1.60	10.97	-2.37
L-2	-45.803555, 168.595161	13/06/2016	6.94	10.72	8.40	223.00	8.00	1.60	90.10	19.20	22.81	0.76	12.46	8.03	1.60	16.89	-8.02
L-3	-45.838009, 168.596191	13/06/2016	7.13	11.63	5.30	226.00	0.00	3.29	114.49	19.71	20.69	0.86	12.97	7.18	2.17	16.97	-5.33
L-4	-45.886304, 168.601856	13/06/2016	7.34	13.35	6.20	202.80	1.00	3.19	126.68	19.36	17.45	0.72	13.27	6.10	1.72	14.02	-5.64
W-1	-45.767164, 168.491821	19/07/2016	7.08	11.03	7.80	91.00	20.00	1.27	305.38	7.87	6.18	0.35	7.50	2.09	0.97	5.68	6.86
W-2	-45.804153, 168.516197	19/07/2016	6.51	10.94	7.20	140.70	49.00	3.31	150.72	12.35	12.02	0.41	8.29	3.33	1.46	8.84	4.87
W-3	-45.839803, 168.533192	19/07/2016	6.60	10.44	7.70	173.50	29.00	4.21	212.58	14.85	16.46	0.49	8.92	4.15	1.78	11.99	-4.83
W-4	-45.876624, 168.528900	19/07/2016	6.78	9.90	7.80	198.30	36.00	4.21	382.71	17.42	18.25	0.59	9.52	5.37	2.28	13.49	-4.16
W-5	-45.898252, 168.549500	19/07/2016	6.85	10.08	7.20	198.10	34.00	4.06	367.24	17.39	17.67	0.62	9.61	5.12	2.20	13.15	-2.47
W-6	-45.925483, 168.592243	19/07/2016	6.90	10.30	7.20	194.70	38.00	4.25	421.38	17.17	17.21	0.60	10.13	4.98	2.99	13.60	-5.51
W-7	-45.944943, 168.660393	19/07/2016	6.88	10.21	7.00	194.60	45.00	4.51	483.24	17.55	17.05	0.57	10.09	4.65	2.21	12.74	-3.37
W-8	-45.987301, 168.80064	19/07/2016	6.91	10.27	7.90	200.30	44.00	4.52	452.31	18.49	18.17	0.55	10.39	4.66	2.10	12.87	-2.79
L-1	-45.783686, 168.557053	19/07/2016	6.65	10.77	8.40	153.10	22.00	4.30	119.79	11.18	14.00	0.43	8.71	3.54	1.55	9.26	-6.08
L-2	-45.803555, 168.595161	19/07/2016	6.79	10.49	8.30	211.30	29.00	4.96	235.78	16.30	20.42	0.74	9.53	5.82	1.64	15.40	-2.41
L-3	-45.838009, 168.596191	19/07/2016	6.40	10.26	6.40	202.30	30.00	5.06	320.85	15.94	20.01	0.65	9.73	5.08	1.93	14.28	-2.77
L-4	-45.886304, 168.601856	19/07/2016	6.94	10.47	6.70	202.00	36.00	5.01	374.98	15.95	19.16	0.62	10.46	5.04	2.09	14.53	-5.77

Appendix B: 2016 trace element chemistry

Site No.	Coordinates	Date	Br	Mn	Fe	B	Al	Ti	V	Cr	Co	Ni	Cu	Zn	As	Zr	Nb	Mo	Cd	Sb	Ta	W	Pb
	Lattitude, longitude		mg/L	mg/L	mg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
W-1	-45.767164, 168.491821	14/02/2016		0.03	0.29		6.83		0.97	0.62	0.67	1.00	1.38	6.15	1.06			1.01	0.55	0.69			0.48
W-2	-45.804153, 168.516197	15/02/2016		0.13	0.30		4.48		0.65	0.37	0.64	1.07	1.34	0.98	0.97			0.61	0.34	0.46			0.30
W-3	-45.839803, 168.533192	15/02/2016		0.10	0.75		4.74		1.06	0.29	0.39	0.97	0.95	0.46	1.85			0.50	0.21	0.30			0.18
W-4	-45.876624, 168.528900	14/02/2016		0.04	0.10		2.69		1.16	0.17	0.19	0.67	0.60	0.30	0.55			0.30	0.12	0.16			0.12
W-5	-45.898252, 168.549500	15/02/2016		0.03	0.11		1.58		0.64	0.12	0.13	0.48	0.40	0.20	0.39			0.23	0.06	0.11			0.05
W-6	-45.925483, 168.592243	14/02/2016		0.01	0.18		3.41		1.13	0.10	0.14	0.38	0.43	0.14	0.55			0.20	0.05	0.08			0.03
W-7	-45.944943, 168.660393	15/02/2016		0.02	0.15		4.34		0.94	0.09	0.13	0.40	0.49	0.53	0.54			0.17	0.04	0.06			0.04
W-8	-45.987301, 168.80064	14/02/2016		0.02	0.16		5.53		1.63	0.07	0.19	0.46	0.71	0.33	0.78			0.15	0.04	0.07			0.03
L-1	-45.783686, 168.557053	14/02/2016		0.48	1.50		27.47		1.42	0.22	0.93	2.01	1.10	0.73	2.04			0.26	0.19	0.08			0.16
L-2	-45.803555, 168.595161	14/02/2016		0.22	0.66		3.68		1.15	0.16	0.26	0.86	0.71	0.73	2.56			0.32	0.02	0.06			0.03
L-3	-45.838009, 168.596191	14/02/2016		0.13	0.85		6.16		1.46	0.11	0.29	0.73	0.47	0.41	2.27			0.18	0.01	0.06			0.06
L-4	-45.886304, 168.601856	15/02/2016		0.02	0.27		3.78		0.75	0.13	0.09	0.26	0.25	0.19	0.52			0.07	0.01	0.03			0.03
E44/0036	-45.867797, 168.550647	15/02/2016		0.00	0.03		0.32		0.35	0.12	0.01	0.69	3.07	10.32	0.07			0.06	0.05	0.01			0.15
W-1	-45.767164, 168.491821	13/03/2016		0.02	0.31	19.87	39.13	1.69	0.29	0.13	0.11	0.44	0.83	115.86	0.39	0.11	0.15	0.16	0.12	0.04	0.10	0.04	0.17
W-2	-45.804153, 168.516197	12/03/2016		0.01	0.08	16.29	21.75	0.31	0.36	0.10	0.23	0.54	1.85	64.62	0.33	0.06	0.09	0.12	0.07	0.04	0.09	0.03	0.07
W-3	-45.839803, 168.533192	13/03/2016	0.02	0.03	0.40	25.51	26.76	0.96	0.45	0.12	0.28	0.64	1.78	40.76	0.60	0.07	0.08	0.13	0.05	0.04	0.09	0.03	0.07
W-4	-45.876624, 168.528900	13/03/2016	0.03	0.02	0.08	18.86	30.99	0.41	0.45	0.12	0.11	0.67	0.62	20.05	0.29	0.03	0.06	0.08	0.09	0.03	0.08	0.02	0.62
W-5	-45.898252, 168.549500	12/03/2016	0.04	0.01	0.07	17.87	5.04	0.43	0.59	0.09	0.09	0.42	0.54	12.20	0.32	0.02	0.05	0.19	0.05	0.03	0.09	0.03	0.01
W-6	-45.925483, 168.592243	12/03/2016	0.05	0.01	0.09	17.42	19.04	0.83	0.74	0.11	0.10	0.43	0.66	52.02	0.38	0.03	0.04	0.11	0.05	0.03	0.08	0.03	0.06
W-7	-45.944943, 168.660393	12/03/2016	0.04	0.02	0.11	17.12	17.26	0.86	0.81	0.07	0.11	0.37	0.71	9.58	0.41	0.04	0.03	0.08	0.04	0.03	0.08	0.03	0.04
W-8	-45.987301, 168.80064	12/03/2016	0.03	0.01	0.10	18.43	5.10	1.00	0.93	0.06	0.14	0.41	0.92	3.66	0.53	0.04	0.03	0.08	1.65	0.02	0.08	0.02	0.03
L-1	-45.783686, 168.557053	13/03/2016	0.03	0.31	1.23	23.20	29.94	3.78	1.03	0.18	0.66	1.18	1.76	11.89	1.51	0.19	0.03	0.17	0.04	0.03	0.08	0.03	0.10
L-2	-45.803555, 168.595161	13/03/2016	0.02	0.04	0.40	98.35	26.22	2.17	1.37	0.23	0.16	0.80	0.99	63.88	1.64	0.11	0.03	0.28	0.14	0.06	0.08	6.67	0.13
L-3	-45.838009, 168.596191	12/03/2016	0.03	0.02	0.35	28.79	18.07	2.34	1.72	0.14	0.23	0.71	0.69	22.90	1.34	0.07	0.03	0.15	0.05	0.04	0.08	0.11	0.21
L-4	-45.886304, 168.601856	13/03/2016	0.05	0.01	0.12	13.22	7.47	0.76	0.71	0.11	0.09	0.24	0.29	19.32	0.68	0.01	0.02	0.07	0.06	0.02	0.08	0.10	0.03
W-1	-45.767164, 168.491821	10/04/2016	0.01	0.01	0.32	11.49	20.54	2.31	0.26	0.10	0.09	0.36	0.78	53.98	0.39	0.11	0.02	0.12	0.07	0.03	0.07	0.05	0.18
W-2	-45.804153, 168.516197	10/04/2016	0.01	0.00	0.18	16.95	12.22	1.45	0.24	0.07	0.25	0.36	3.09	6.66	0.34	0.08	0.02	0.05	0.32	0.02	0.06	0.03	0.02
W-3	-45.839803, 168.533192	9/04/2016	0.01	0.01	0.27	16.22	14.94	2.49	0.42	0.08	0.28	0.41	4.56	4.97	0.37	0.07	0.02	0.10	0.14	0.03	0.06	0.03	0.05
W-4	-45.876624, 168.528900	9/04/2016	0.02	0.01	0.11	21.26	9.11	1.14	0.60	0.11	0.27	0.65	4.15	10.43	0.37	0.04	0.01	0.12	0.18	0.04	0.06	0.05	0.07
W-5	-45.898252, 168.549500	9/04/2016	0.03	0.01	0.10	18.21	6.80	0.72	0.51	0.08	0.19	0.47	2.04	5.30	0.32	0.03	0.01	0.07	0.44	0.02	0.06	0.03	0.03
W-6	-45.925483, 168.592243	9/04/2016	0.03	0.01	0.06	15.52	6.80	0.37	0.60	0.06	0.12	0.32	0.70	5.44	0.32	0.02	0.01	0.04	0.02	0.01	0.05	0.02	0.01
W-7	-45.944943, 168.660393	9/04/2016	0.03	0.03	0.08	18.34	5.06	0.72	0.73	0.07	0.12	0.38	0.52	1.84	0.38	0.02	0.01	0.07	0.04	0.02	0.06	0.03	0.01
W-8	-45.987301, 168.80064	9/04/2016	0.03	0.02	0.08	14.94	3.60	0.69	0.82	0.05	0.11	0.37	0.89	3.40	0.42	0.05	0.17	0.06	0.02	0.06	0.07	0.05	0.03
L-1	-45.783686, 168.557053	10/04/2016	0.02	0.06	0.92	20.79	24.35	2.94	0.78	0.13	0.26	0.74	1.03	2.18	0.98	0.17	0.12	0.08	0.02	0.03	0.07	0.05	0.08
L-2	-45.803555, 168.595161	10/04/2016	0.02	0.04	0.37	55.21	7.52	1.49	1.54	0.15	0.24	0.63	0.63	6.02	1.37	0.11	0.09	0.18	0.04	0.04	0.06	0.04	0.04
L-3	-45.838009, 168.596191	9/04/2016	0.04	0.03	0.13	67.14	5.90	0.88	1.83	0.11	0.19	0.67	0.88	9.04	2.46	0.07	0.07	1.81	0.87	0.17	0.07	0.06	0.03
L-4	-45.886304, 168.601856	9/04/2016	0.04	0.01	0.08	13.03	4.99	0.45	0.66	0.21	0.06	0.27	0.37	9.45	0.40	0.02	0.05	0.11	0.12	0.02	0.06	0.04	0.02

Site No.	Coordinates	Date	Br	Mn	Fe	B	Al	Ti	V	Cr	Co	Ni	Cu	Zn	As	Zr	Nb	Mo	Cd	Sb	Ta	W	Pb
	Lattitude, longitude		mg/L	mg/L	mg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
W-1	-45.767164, 168.491821	22/05/2016	0.02	0.04	0.16	13.35	50.26	4.72	0.31	0.10	0.16	0.31	1.34	6.98	0.26	0.16	0.05	0.38	1.42	0.04	0.05	0.02	0.02
W-2	-45.804153, 168.516197	21/05/2016	0.03	0.01	0.11	17.19	44.26	4.92	0.32	0.11	0.18	0.40	2.66	4.42	0.26	0.12	0.04	0.07	0.03	0.02	0.05	0.02	0.02
W-3	-45.839803, 168.533192	22/05/2016	0.03	0.01	0.12	22.94	34.89	3.84	0.36	0.15	0.19	0.59	3.26	11.99	0.34	0.13	0.03	1.24	15.39	0.13	0.06	0.03	0.08
W-4	-45.876624, 168.528900	22/05/2016	0.04	0.01	0.08	25.22	22.84	3.16	0.48	0.12	0.15	0.62	1.82	23.32	0.32	0.09	0.03	0.37	1.94	0.04	0.05	0.03	0.02
W-5	-45.898252, 168.549500	21/05/2016	0.04	0.01	0.08	27.03	33.73	4.81	0.53	0.15	0.15	0.69	1.68	15.92	0.33	0.13	0.03	0.29	14.95	0.04	0.05	0.03	0.06
W-6	-45.925483, 168.592243	21/05/2016	0.07	0.01	0.09	27.63	23.45	4.01	0.60	0.13	0.16	0.52	1.42	7.39	0.34	0.09	0.03	0.09	0.39	0.02	0.05	0.03	0.01
W-7	-45.944943, 168.660393	21/05/2016	0.05	0.01	0.11	28.21	32.37	5.43	0.66	0.13	0.16	0.52	1.17	2.48	0.35	0.15	0.03	0.11	0.40	0.02	0.05	0.02	0.02
W-8	-45.987301, 168.80064	21/05/2016	0.05	0.02	0.12	25.48	46.31	7.56	0.72	0.15	0.17	0.57	1.53	4.96	0.37	0.19	0.03	0.20	0.48	0.03	0.05	0.02	0.07
L-1	-45.783686, 168.557053	22/05/2016	0.04	0.05	0.24	27.71	35.71	2.95	0.30	0.13	0.24	0.74	2.00	3.62	0.36	0.11	0.02	0.27	3.83	0.04	0.04	0.02	0.12
L-2	-45.803555, 168.595161	22/05/2016	0.04	0.03	0.11	40.22	56.81	6.64	1.06	0.22	0.22	0.62	1.56	9.23	0.44	0.13	0.03	1.58	5.03	0.40	0.05	0.04	0.05
L-3	-45.838009, 168.596191	21/05/2016	0.05	0.01	0.10	40.82	40.03	5.39	0.66	0.16	0.16	0.56	1.28	0.88	0.42	0.11	0.02	0.07	0.01	0.04	0.05	0.04	0.01
L-4	-45.886304, 168.601856	21/05/2016	0.05	0.01	0.09	33.42	35.22	5.67	0.69	0.19	0.15	0.57	1.44	22.86	0.40	0.11	0.02	0.24	8.36	0.05	0.05	0.02	0.10
W-1	-45.767164, 168.491821	13/06/2016	0.03	0.02	0.24	16.23	26.85	2.64	0.25	0.08	0.10	0.28	0.63	7.48	0.25	0.10	0.02	0.16	0.68	0.03	0.04	0.03	0.01
W-2	-45.804153, 168.516197	13/06/2016	0.04	0.01	0.11	21.51	17.45	1.38	0.23	0.07	0.17	0.47	2.67	7.83	0.22	0.05	0.02	0.09	0.17	0.02	0.04	0.02	0.01
W-3	-45.839803, 168.533192	13/06/2016	0.02	0.04	0.14	28.64	26.63	2.84	0.33	0.12	0.27	0.94	2.42	48.09	0.31	0.10	0.02	0.73	4.37	0.07	0.05	0.02	0.04
W-4	-45.876624, 168.528900	13/06/2016	0.03	0.02	0.07	26.80	19.94	0.66	0.48	0.13	0.16	0.94	1.34	32.19	0.31	0.10	0.19	4.72	1.44	0.10	0.06	0.06	0.06
W-5	-45.898252, 168.549500	13/06/2016	0.07	0.02	0.07	27.84	17.42	0.52	0.47	0.15	0.16	0.92	1.48	43.50	0.34	0.07	0.12	0.23	3.24	0.04	0.06	0.05	0.18
W-6	-45.925483, 168.592243	13/06/2016	0.03	0.02	0.09	27.65	11.50	0.65	0.46	0.13	0.16	0.66	1.37	9.23	0.30	0.06	0.09	0.17	0.98	0.03	0.05	0.03	0.14
W-7	-45.944943, 168.660393	13/06/2016	0.04	0.02	0.11	27.29	13.47	0.78	0.47	0.11	0.15	0.63	1.60	15.50	0.32	0.06	0.07	0.20	0.08	0.03	0.05	0.03	0.00
W-8	-45.987301, 168.80064	13/06/2016	0.04	0.01	0.12	29.12	13.33	0.53	0.47	0.10	0.13	0.57	1.64	14.14	0.34	0.06	0.06	0.19	3.48	0.06	0.05	0.03	0.05
L-1	-45.783686, 168.557053	13/06/2016	0.04	0.07	0.39	26.78	18.19	0.42	0.27	0.11	0.28	0.89	1.06	15.49	0.37	0.07	0.05	0.44	0.70	0.06	0.05	0.05	0.03
L-2	-45.803555, 168.595161	13/06/2016	0.04	0.02	0.10	41.26	27.36	0.99	0.76	0.22	0.17	0.68	1.49	37.15	0.38	0.06	0.04	0.41	5.80	0.08	0.05	0.03	0.19
L-3	-45.838009, 168.596191	13/06/2016	0.05	0.01	0.11	36.52	17.05	1.04	0.49	0.16	0.16	0.62	1.15	2.97	0.39	0.07	0.04	0.08	0.07	0.03	0.05	0.03	0.02
L-4	-45.886304, 168.601856	13/06/2016	0.04	0.01	0.10	26.40	14.88	0.88	0.50	0.16	0.14	0.54	0.88	13.28	0.33	0.05	0.03	0.12	0.47	0.05	0.04	0.02	0.06
W-1	-45.767164, 168.491821	19/07/2016	0.01	0.01	0.09	11.14	54.58	1.25	0.26	0.10	0.13	0.28	1.02	1.05	0.18	0.11	0.03	0.07	0.15	0.02	0.05	0.02	0.02
W-2	-45.804153, 168.516197	19/07/2016	0.02	0.01	0.07	16.25	58.01	1.91	0.27	0.15	0.18	0.48	1.93	4.08	0.20	0.16	0.02	0.32	3.96	0.05	0.04	0.01	0.02
W-3	-45.839803, 168.533192	19/07/2016	0.02	0.02	0.11	22.59	124.95	4.94	0.44	0.21	0.38	1.05	2.16	7.81	0.32	0.21	0.02	0.38	0.23	0.07	0.04	0.02	0.06
W-4	-45.876624, 168.528900	19/07/2016	0.02	0.03	0.11	26.04	128.26	6.31	0.68	0.24	0.30	1.38	2.24	7.37	0.37	0.22	0.03	0.15	1.78	0.03	0.04	0.01	0.08
W-5	-45.898252, 168.549500	19/07/2016	0.03	0.03	0.12	26.60	145.86	8.69	0.69	0.24	0.27	1.23	2.00	2.76	0.39	0.34	0.03	0.07	0.74	0.03	0.04	0.02	0.06
W-6	-45.925483, 168.592243	19/07/2016	0.02	0.03	0.13	27.15	141.66	7.69	0.71	0.25	0.27	1.28	2.08	10.04	0.38	0.22	0.03	3.08	7.41	0.26	0.04	0.03	0.10
W-7	-45.944943, 168.660393	19/07/2016	0.03	0.03	0.11	26.56	99.20	4.52	0.65	0.21	0.24	0.95	2.64	5.27	0.54	0.17	0.02	1.03	49.42	0.06	0.04	0.02	0.05
W-8	-45.987301, 168.80064	19/07/2016	0.03	0.03	0.13	27.01	125.68	5.25	0.74	0.20	0.26	0.97	1.91	5.34	0.39	0.20	0.02	0.12	0.10	0.03	0.04	0.02	0.07
L-1	-45.783686, 168.557053	19/07/2016	0.01	0.03	0.09	26.93	64.19	1.65	0.26	0.16	0.24	0.76	1.55	7.45	0.27	0.11	0.01	0.16	0.14	0.06	0.04	0.02	0.04
L-2	-45.803555, 168.595161	19/07/2016	0.02	0.03	0.09	31.63	81.55	4.46	0.79	0.24	0.24	0.72	2.11	4.89	0.36	0.13	0.02	0.14	0.47	0.03	0.04	0.02	0.14
L-3	-45.838009, 168.596191	19/07/2016	0.01	0.02	0.10	31.57	88.59	6.02	0.56	0.24	0.23	0.79	1.90	5.62	0.38	0.27	0.15	0.22	0.79	0.13	0.06	0.10	0.04
L-4	-45.886304, 168.601856	19/07/2016	0.03	0.02	0.11	32.96	83.94	3.86	0.61	0.27	0.25	0.80	1.94	4.55	0.41	0.19	0.08	0.12	5.39	0.06	0.05	0.05	0.05

Appendix c: 2016 stable isotope data

Site code	Date	Coordinates (latitude, longitude)	$\delta^{13}C$ (‰ V-PDB)	$\delta^{13}C$ (stdev)	$\delta^{18}O$ (‰ V-PDB)	$\delta^{18}O$ (stdev)	mMoles C per litre	$\delta^{18}O$ (‰ V-SMOW)	$\delta^{18}O$ (stdev)	$\delta^{2}H$ (‰ V-SMOW)	$\delta^{2}H$ (stdev)	*d-excess*
W-1	14/02/2016	-45.767164, 168.491821	-12.10	0.12	-9.54	0.11	0.85	-7.29	0.20	-52.33	0.65	5.98
W-2	15/02/2016	-45.804153, 168.516197	-14.86	0.09	-8.28	0.18	1.16	-6.62	0.08	-47.90	0.16	5.08
W-3	15/02/2016	-45.839803, 168.533192	-15.24	0.08	-7.58	0.38	1.79	-6.59	0.16	-49.53	0.92	3.16
W-4	14/02/2016	-45.876624, 168.528900	-14.54	0.10	-9.14	0.15	1.17	-7.40	0.03	-53.05	0.00	6.11
W-5	15/02/2016	-45.898252, 168.549500	-16.58	0.04	-8.40	0.03	1.22	-7.05	0.09	-52.67	0.57	3.74
W-6	14/02/2016	-45.925483, 168.592243	-15.00	0.02	-9.07	0.01	0.92	-7.04	0.03	-52.53	0.46	3.82
W-7	15/02/2016	-45.944943, 168.660393	-16.15	0.02	-8.92	0.08	1.20	-6.97	0.18	-51.62	0.04	4.17
W-8	14/02/2016	-45.987301, 168.80064	-15.55	0.10	-8.38	0.00	1.03	-6.60	0.10	-49.92	0.07	2.85
L-1	14/02/2016	-45.783686, 168.557053	-14.77	0.01	-9.23	0.02	0.81	-7.63	0.08	-55.37	0.26	5.65
L-2	14/02/2016	-45.803555, 168.595161	-13.27	0.00	-7.18	0.17	1.74	-6.46	0.02	-49.93	0.05	1.75
L-3	14/02/2016	-45.838009, 168.596191	-16.33	0.15	-6.00	2.17	2.95	-6.65	0.06	-49.15	1.00	4.05
L-4	15/02/2016	-45.886304, 168.601856	-17.70	0.00	-7.21	0.31	1.90	-6.18	0.02	-46.42	0.61	3.04
E44/0036	15/02/2016	-45.867797, 168.550647	-22.61	0.03	-8.23	0.07	1.22	-7.41	0.10	-53.73	0.05	5.59
W-1	13/03/2016	-45.767164, 168.491821	-12.42	0.14	-8.55	0.06	0.75	-7.69	0.08	-52.10	0.45	9.40
W-2	12/03/2016	-45.804153, 168.516197	-14.77	0.02	-8.04	0.06	0.54	-7.03	0.12	-48.56	0.30	7.72
W-3	13/03/2016	-45.839803, 168.533192	-14.85	0.00	-7.71	0.03	1.07	-6.75	0.06	-47.51	0.76	6.48
W-4	13/03/2016	-45.876624, 168.528900	-16.31	0.06	-8.51	0.05	1.22	-7.36	0.08	-51.12	0.24	7.75
W-5	12/03/2016	-45.898252, 168.549500	-14.37	0.02	-8.36	0.04	1.05	-7.39	0.11	-52.26	0.23	6.83
W-6	12/03/2016	-45.925483, 168.592243	-13.74	0.02	-8.50	0.04	0.88	-7.30	0.13	-51.63	0.33	6.81
W-7	12/03/2016	-45.944943, 168.660393	-13.78	0.03	-8.19	0.05	1.17	-7.19	0.07	-50.39	0.24	7.14
W-8	12/03/2016	-45.987301, 168.80064	-14.46	0.01	-7.52	0.06	1.18	-6.59	0.14	-48.03	0.06	4.72
L-1	13/03/2016	-45.783686, 168.557053	-17.05	0.01	-7.53	0.01	1.39	-6.59	0.14	-45.16	0.06	7.52
L-2	13/03/2016	-45.803555, 168.595161	-16.50		-6.66		2.36	-6.90	0.12	-48.91	0.81	6.25
L-3	12/03/2016	-45.838009, 168.596191	-15.04	0.00	-7.20	0.01	1.35	-5.75	0.15	-43.79	1.08	2.23
L-4	13/03/2016	-45.886304, 168.601856	-17.17	0.09	-8.93	0.04	0.92	-7.46	0.18	-53.32	1.28	6.33
W-1	10/04/2016	-45.767164, 168.491821	-10.64	0.02	-9.32	0.01	0.52	-7.66	0.02	-52.03	0.10	9.23
W-2	10/04/2016	-45.804153, 168.516197	-11.79	0.03	-8.88	0.10	0.60	-8.12	0.02	-52.99	0.17	11.98
W-3	9/04/2016	-45.839803, 168.533192	-10.32	0.03	-8.72	0.00	0.60	-8.22	0.03	-52.94	0.98	12.82
W-4	9/04/2016	-45.876624, 168.528900	-12.88	0.00	-8.89	0.06	0.82	-8.22	0.11	-53.90	1.31	11.84
W-5	9/04/2016	-45.898252, 168.549500	-14.75	0.01	-8.76	0.01	0.84	-7.66	0.10	-52.60	0.26	8.71
W-6	9/04/2016	-45.925483, 168.592243	-14.66	0.00	-8.79	0.05	0.82	-7.47	0.16	-52.03	0.80	7.74
W-7	9/04/2016	-45.944943, 168.660393	-14.87	0.01	-8.66	0.01	0.95	-7.62	0.10	-52.28	0.51	8.65
W-8	9/04/2016	-45.987301, 168.80064	-14.10	0.08	-8.80	0.04	1.03	-7.88	0.22	-54.78	0.91	8.24
L-1	10/04/2016	-45.783686, 168.557053	-14.96	0.05	-8.36	0.09	0.91	-7.29	0.05	-48.58	0.79	9.76
L-2	10/04/2016	-45.803555, 168.595161	-16.49	0.03	-5.65	0.06	2.12	-7.31	0.04	-50.96	0.12	7.48
L-3	9/04/2016	-45.838009, 168.596191	-14.56	0.04	-6.09	0.02	2.08	-7.20	0.11	-50.66	0.06	6.95
L-4	9/04/2016	-45.886304, 168.601856	-15.02	0.03	-9.08	0.01	0.70	-7.83	0.07	-54.20	0.41	8.42
W-1	22/05/2016	-45.767164, 168.491821	-13.99	0.02	-8.19	0.03	0.85	-7.97	0.06	-51.57	0.59	12.20
W-2	21/05/2016	-45.804153, 168.516197	-14.22	0.05	-8.20	0.02	0.77	-7.73	0.16	-52.02	0.24	9.83
W-3	22/05/2016	-45.839803, 168.533192	-14.40	0.04	-8.07	0.05	0.82	-7.79	0.02	-50.43	0.26	11.92
W-4	22/05/2016	-45.876624, 168.528900	-16.92	0.03	-8.18	0.11	1.12	-7.91	0.05	-51.82	0.40	11.48
W-5	21/05/2016	-45.898252, 168.549500	-15.04	0.03	-8.32	0.08	1.03	-7.86	0.07	-51.15	0.29	11.74
W-6	21/05/2016	-45.925483, 168.592243	-14.26	0.03	-8.02	0.07	0.99	-7.65	0.18	-51.74	0.60	9.47
W-7	21/05/2016	-45.944943, 168.660393	-13.66	0.02	-7.88	0.08	1.00	-7.60	0.11	-49.77	0.27	11.04
W-8	21/05/2016	-45.987301, 168.80064	-12.89	0.02	-8.02	0.02	0.97	-7.61	0.04	-50.10	0.81	10.79
L-1	22/05/2016	-45.783686, 168.557053	-16.94	0.01	-8.21	0.01	0.94	-7.44	0.01	-49.62	0.22	9.90
L-2	22/05/2016	-45.803555, 168.595161	-18.03	0.03	-8.10	0.06	1.65	-7.50	0.00	-49.66	0.12	10.36
L-3	21/05/2016	-45.838009, 168.596191	-15.11	0.01	-8.01	0.02	1.03	-7.47	0.10	-49.80	0.43	9.93
L-4	21/05/2016	-45.886304, 168.601856	-14.91	0.02	-8.18	0.06	1.05	-7.61	0.05	-50.94	0.38	9.91
W-1	13/06/2016	-45.767164, 168.491821	-12.65	0.12	-8.82	0.11	0.84	-7.93	0.01	-53.34	0.11	10.07
W-2	13/06/2016	-45.804153, 168.516197	-13.29	0.02	-8.75	0.04	0.74	-7.72	0.07	-51.89	0.25	8.05
W-3	13/06/2016	-45.839803, 168.533192	-13.97	0.04	-8.64	0.07	0.83	-7.61	0.07	-51.94	0.73	8.93
W-4	13/06/2016	-45.876624, 168.528900	-16.26	0.03	-8.71	0.06	1.13	-7.62	0.02	-52.65	0.09	8.34
W-5	13/06/2016	-45.898252, 168.549500	-15.93	0.06	-8.50	0.09	1.15	-7.51	0.09	-52.47	0.61	7.59
W-6	13/06/2016	-45.925483, 168.592243	-15.60	0.06	-8.52	0.13	1.12	-7.32	0.11	-52.39	0.69	6.17
W-7	13/06/2016	-45.944943, 168.660393	-14.60	0.01	-8.39	0.07	1.08	-7.42	0.07	-51.60	0.56	7.76
W-8	13/06/2016	-45.987301, 168.80064	-13.89	0.05	-8.41	0.07	1.15	-7.50	0.02	-51.53	0.04	8.44
L-1	13/06/2016	-45.783686, 168.557053	-14.70	0.08	-8.43	0.18	0.92	-7.27	0.14	-51.12	0.09	7.06
L-2	13/06/2016	-45.803555, 168.595161	-15.92	0.04	-8.27	0.06	1.49	-7.39	0.10	-51.82	0.12	7.32
L-3	13/06/2016	-45.838009, 168.596191	-15.34	0.06	-8.21	0.06	1.20	-7.28	0.10	-51.41	1.18	6.80
L-4	13/06/2016	-45.886304, 168.601856	-14.27	0.03	-8.41	0.13	1.05	-7.51	0.07	-53.08	0.43	7.02
W-1	19/07/2016	-45.767164, 168.491821	-13.80	0.13	-8.82	0.19	0.68	-8.29	0.04	-55.19	0.19	11.17
W-2	19/07/2016	-45.804153, 168.516197	-16.36	0.04	-8.52	0.09	0.77	-8.07	0.06	-53.64	0.19	10.90
W-3	19/07/2016	-45.839803, 168.533192	-18.36	0.02	-8.18	0.06	1.15	-7.81	0.11	-52.61	0.46	9.85
W-4	19/07/2016	-45.876624, 168.528900	-18.09	0.02	-8.15	0.07	1.11	-7.77	0.07	-52.40	0.37	9.74
W-5	19/07/2016	-45.898252, 168.549500	-17.78	0.06	-8.23	0.05	1.06	-7.68	0.10	-51.53	0.06	9.88
W-6	19/07/2016	-45.925483, 168.592243	-17.55	0.08	-8.16	0.14	1.09	-7.64	0.14	-51.73	0.28	9.38
W-7	19/07/2016	-45.944943, 168.660393	-17.62	0.08	-8.13	0.04	1.05	-7.60	0.01	-51.64	0.03	9.17
W-8	19/07/2016	-45.987301, 168.80064	-15.96	0.06	-7.93	0.08	0.96	-7.71	0.12	-50.84	0.43	10.82
L-1	19/07/2016	-45.783686, 168.557053	-17.95	0.03	-8.21	0.02	0.82	-7.91	0.02	-52.40	0.30	10.89
L-2	19/07/2016	-45.803555, 168.595161	-16.73	0.07	-8.10	0.01	1.30	-7.78	0.13	-52.57	0.72	9.64
L-3	19/07/2016	-45.838009, 168.596191	-16.66	0.03	-8.20	0.13	0.87	-7.62	0.07	-52.50	0.35	8.48
L-4	19/07/2016	-45.886304, 168.601856	-17.91	0.11	-8.25	0.09	1.16	-7.70	0.07	-52.11	0.30	9.53